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A COMPARISON OF CERTAIN ELECTRICAL PROPERTIES ORDINARY AND URANIUM LEAD

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Communicated, June 17, 1919

A comparison of the physical properties of chemical isotopes is significance because of the light it may throw on the correspond mechanisms. Comparisons of the properties of ordinary and uran lead have hitherto been made with respect to the atomic volume,[1] t moelectric quality,[2] and emission spectra.[3] No differences have b detected, except possibly a very slight shift in one of the spectrum li It is not to be expected that large differences exist with regard to o

fied ordinary lead. The radio-active lead was from Australian carnotite, and showed an atomic weight of 206.34, which is therefore 0.41% lower than that of ordinary lead. The theoretical and experimental value for the atomic weight of the pure end product of the disintegration of uranium is 206.08, so that this sample was probably composed of 76% pure isotope and 24% ordinary lead. The radio active lead contained not over 5 parts in 100,000 of impurity, mostly silver, and the ordinary lead was a trifle less pure, showing also a trace of copper. For the experiments both these samples were formed into wire 0.035 cm. in diameter by cold extrusion through a steel die. The samples were cast into ingots ready for extrusion by Professor Richards, who melted them in hydrogen and then continued the fusion for ten minutes in vacuum.

The measurements recorded here are comparisons of the pressure coefficient of electrical resistance, temperature coefficient of resistance, and specific resistance. The comparison of pressure coefficient of electrical resistance was made with more accuracy than the other measurements because a specially adapted apparatus designed for another purpose was available.

In order to compare the pressure coefficients, approximately equal lengths of the two varieties of lead were wound non-inductively on either end of a bone core, which was placed in the pressure chamber. The two terminals of each wire were soldered to independent leads which were brought through the walls of the pressure chamber through an insulating plug of a design essentially like that previously described,[5] except that there were three, instead of one, insulated stems through the plug. The two wires were made the two extension coils of a Carey Foster bridge. In this way the difference of the pressure effects on the two coils could be measured. The absolute value of the pressure effect on ordinary lead had been previously determined with sufficient accuracy.[6] The apparatus for producing pressure was the same as that previously described.[5]

Readings were made to 12,000 kgm./cm.^{2} at 1000 kgm. intervals, with increasing and decreasing pressure, and at two temperatures, 25° and 85°. An independent set of readings was made to determine the effect of pressure on the resistance of the leads, which turned out to be almost negligible. At 25° the decreases of resistance of the two kinds of lead under 12,000 kgm. were the same within 0.02% of the total decrease, and at 85° within 0.03%. Assuming that the possible error

instrumental error in the readings would have been 0.04%. agreement is therefore as close as could be expected. At press lower than 12,000 the agreement of the readings was also always wi possible instrumental errors.

The temperature coefficients were compared by comparing the sistances at atmospheric pressure at 25° and 85°, while still woun the same bone core as was used for the pressure measurements. this range the temperature coefficients differed by 0.06% of themse This is slightly greater than the possible instrumental error, bu less than possible discrepancies due to differences of handling w I have previously found in different lengths from the same samp ordinary lead.

The specific resistances were compared by comparing the a resistances of the samples already measured. Correction for equalities of dimensions was made by measuring the length of sample and its weight, and from these computing the average cross tion assuming that the densities were directly proportional to atomic weights.[1] In order to measure the length, the wire had t cut from the core, unwound, and straightened. Because of the chanical softness of lead, this is a difficult operation without erro that the comparison of specific resistance is less accurate than of sure or temperature coefficient. Two independent comparison specific resistance were made. The discrepancies of these two com sons differed in sign; the average of the two comparisons showe agreement of specific resistance of 0.06%.

Conclusion.—These measurements establish that any differenc tween the pressure coefficient of resistance, temperature coeff and specific resistance is at least many fold less than the diffe of the atomic weights. It seems indicated with a high degree of p bility that the same conclusion will be found also to apply to the pressibility and thermal expansion. The results fortify the poi view embodied in recent theories of electrical resistance that the esses involved in electrical conduction take place in the outer p the atomic structure.

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A CRITICAL THERMODYNAMIC DISCUSSION OF THE VOLTA, THERMO-ELECTRIC AND THERMIONIC EFFECTS.

A CRITICAL THERMODYNAMIC DISCUSSION OF THE VOLTA, THERMO-ELECTRIC AND THERMIONIC EFFECTS.

By P. W. Bridgman.

Synopsis.

In this paper the various relations between the Volta effect, thermo-electric effects, and thermionic effects are critically discussed from the general view point of thermodynamics, avoiding assumptions involving special mechanisms. The ordinary concept of an impressed E.M.F. is found inadequate, and a general definition is proposed, competent to include systems in which the force driving electricity has not the character of a spatially distributed field of force. A thermodynamic proof, dispensing with all special assumptions, is given for a formula for the temperature coefficient of the Volta effect originally given by Lorentz and Kelvin. This temperature coefficient involves a surface heat, the existence of which has not yet been established experimentally, and the possibility of which is usually overlooked. It is shown that Richardson has neglected this surface heat, and that the formula of Lorentz and Kelvin may be deduced also from the phenomena of thermionic emission when the surface heat is taken into account. Formulas are deduced connecting the latent heat of vaporization of electrons, surface heat, surface E.M.F., surface potential jump, Thomson heat, E.M.F. and potential gradient. It is shown that in general local heat, potential difference, and E.M.F. cannot be equal to each other. An expression is found from thermionic considerations for the Volta difference of potential between two parts of the same unequally heated metal, and the possibility suggested of using this effect in determining the hypothetical surface heat. It is shown that it is almost certain that in an unequally heated metal there are currents continuously flowing in closed circuits through the metal and the surrounding electron gas. It is shown that the Volta law of tensions must be capable of extension to include the local potential jumps and E.M.F.'s, although these are not susceptible of direct measurement. Finally, expressions are deduced for the effects of pressure and change of state on the Volta contact difference of potential. These involve the change of volume with surface charge and the effect of surface charge on melting pressure; effects for which no search has been made yet experimentally.

Introduction.

In a recent paper I have described the effect of pressure on the thermo electric properties of metals. In an effort to obtain as much information as possible from the results I later undertook to discuss the relations of thermo-electric phenomena to the Volta effect and the phenomena of thermionic emission. This discussion proved to be difficult because of the great differences of opinion

the nature of the Volta potential difference, and a locally absorbed he
are all involved and discouragingly confuse the issues. Nearly
previous discussions of these matters have involved special assumptio
as to the relations of these phenomena. It is a question to what exte
the correctness of the previous results depends on the special assumptio
In order that the discussion of the effects of high pressures might be fr
from such elements of uncertainty, I have started at the beginning a
examined the whole field from a single point of view. In this examin
tion I have tried to avoid every special assumption, for instance assumi
neither that the jump of potential at two metals in contact is equal
the Volta contact difference, as does Kelvin, nor that it is equal to t
Peltier heat, as do Heaviside and Richardson. The methods employ
in this examination are largely the general methods of thermodynami
in this way the assumption of special mechanisms is avoided. T
results of this critical examination constitute this paper.

It turns out that a number of the previous results are unaffected
the special assumptions under which they were developed. In Richar
son's work, however, I believe that I have discovered an effect whi
he has neglected, and which will bring his formula for the temperatu
coefficient of Volta contact difference of potential into agreement with
formula previously given by Lorentz and later by Kelvin. The effe
neglected is a hypothetical surface heat, whose existence has not y
been searched for experimentally and whose magnitude may well l
for any information we have at present, large enough to essentia
modify many of the thermionic formulas. In the following a numb
of thermionic formulas are given as modified by this effect. In additio
the specific relations are developed between the local E.M.F.'s, lo
potential jumps, and local heats which express the necessary relatio
when these quantities are not assumed respectively equal, as has f
quently been done previously. A connection is found between t
surface heat and the Volta difference of potential between two parts
the same unequally heated metal. Finally the effects of pressure a
change of state on the various effects are discussed from the point
view of thermodynamics.

The Concept of Impressed E.M.F.

It is in the first place necessary to examine the concept of an impress
E.M.F., because with the discovery of new facts, such as those of electr
emission, the old concepts have become inadequate. As commo
understood a part of the E.M.F. between two points in a station

line integral of the "electric" force. The electric force is to be computed in the classical way from the field equations. In addition to forces of electro-magnetic origin, however, it is necessary to recognize the presence of non-electro-magnetic forces acting on electricity. For instance, in an electron gas in which there is a pressure gradient, the pressure gradient gives rise to a non-electro-magnetic force acting on electricity. Such forces may be specifically introduced into our equations and are called "impressed forces," in the same way that impressed forces are introduced into mechanics. In an electrical system in which there are impressed forces it is usual to recognize the presence of an impressed E.M.F.; it is this concept of impressed E.M.F. and its relation to that of impressed force which requires examination.

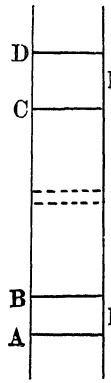


Fig. 1.

It is usual to connect in a simple way the impressed forces with the impressed E.M.F. A careful exposition of this point of view will be found in Abraham (2), for example. Consider a conductor in which the electricity is in equilibrium under the action of the electric and the impressed forces. We may denote the electric force by E^s and the impressed force by E^e. Then since there is equilibrium, $E^s+E^e=0$. The impressed E.M.F. between two points in such a system is usually defined as $\int E^e ds$. This analysis of the situation is inadequate, however, as the following considerations will show.

Consider the behavior of a gas in a field of force, such as an ordinary gas in a gravitational field or an electron gas in a potential field. Let a portion of the gas originally at AB (Fig. 1) rise isothermally under equilibrium conditions to CD. The work done by the pressures acting across the boundaries in this displacement is zero. This may be proved by a direct integration, or may be simply seen as follows: Consider the work done across the surfaces during a displacement shown by the dotted lines. The work done by the top surface in moving through this displacement will be exactly neutralized at some later instant by the work received by the bottom surface in moving through the same displacement. Hence no net work will be done by the top and bottom surfaces together in the region CB. The total work of the operation will be that received by the bottom surface in moving from A to B minus that done by the top surface in moving from C to D. The first is p_1v_1, and the second is p_2v_2. But $p_1v_1 = p_2v_2$ (isothermal). Hence no net work is done by the

We are here confronted with a paradox, the gravitational force bei always equilibrated by other forces, but the gravitational force doi work during a given displacement while the others do none. (There here no contradiction of the first law of thermodynamics, the ener required to increase the potential energy of position being provided heat inflow as the gas expands isothermally.) The solution of t paradox lies in the observation that the two forces concerned, the gra tational force and the equilibrating forces, are entirely different in natu One is a body force, and the other a differential pressure, of the nature the stresses in an elastic solid. One would never think of saying tha gravitational force and the stresses called into play by it in an elas solid were equal to each other. Still less can one speak of the line integ of the equilibrating forces; such an expression can have only a form meaning and cannot be equal to the work done by such forces duri the given displacement.

It follows that the concept of an impressed E.M.F. as the line integ of a non-electric force has a chance of being correct only in those ca in which the non-electric force is in its nature a body force, like t forces of the electrostatic field.

Before defining precisely what we shall mean by an impressed E.M it is to be noticed that the idea is a relative one, as in all cases of ener transformation. Consider a closed circuit, for example, in which eve one is pretty well agreed in calling the impressed E.M.F. the work do when unit quantity of electricity flows around the circuit. But wo done on what? If the circuit consists of a dynamo and a motor, sh we mean the total work done by the motor, or the net work of dyna and motor together? It must be obvious that to give impressed E.M a precise meaning we must divide our universe into two parts; one is t part in which the action takes place which we specify as E.M.F., a the other we shall call the "outside" part, on which the action of t impressed E.M.F. is expended. We could therefore say that the i pressed E.M.F. of a closed circuit is the energy, including heat, delive to "outside" agencies when unit quantity of electricity flows arou the circuit. In the example above, the motor may be taken as the o side agency to which energy is delivered by the E.M.F. of the dyna when unit quantity flows.

With this recognition that impressed E.M.F. involves the specifi tion of some outside agency to receive energy, and that the magnitu of the E.M.F. will depend on the choice of the outside agency, we def

in the direction B to A is the energy delivered to outside agencies per unit quantity when positive electricity passes from B to A, plus the increase of energy of the electricity, including in this both increase of energy in the electro-magnetic field and intrinsic energy (as for example in an electron gas)." This reduces to the ordinary definition for a closed circuit, and for a battery on open circuit with terminals of the same metal reduces to the electrostatic potential difference of the terminals, as it should. By "energy per unit quantity" as used in the definition is to be understood the limit of the ratio of energy to quantity for quantities sufficiently large. That is, the distinction emphasized by Lorentz between "mathematical" and "physical" infinitesimals is to be kept in mind, and in the limiting process contemplated in this definition the "physical" infinitesimal quantity of electricity is large enough to include many electrons.

The discussion of this paper will be largely concerned with thermo-electric processes, in which heat energy is converted into electrical energy. This point of view demands that all the heat processes connected with this conversion, except the irreversible Joulean heat, be ascribed to the internal part of the system whose E.M.F. is discussed, as opposed to the outside agencies which receive the converted energy. In particular, the reversible Peltier heat in a thermo-electric circuit is not to be treated as energy delivered to an "outside" source.

These views of impressed E.M.F. are not in agreement with those commonly held. Consider, for instance, the example of the electric double layers which may exist on the surface of separation of metal and ether. The existence of such layers demands a jump in the electrostatic potential. It is common to say that in this double layer there is an equal and opposite impressed E.M.F.[1] The argument is that otherwise the electricity in the double layers could not be in equilibrium. But the argument is not valid if the non-electrical forces are different in nature from the electrostatic forces. We have seen in one special case that the non-electrostatic forces may be like the stresses of an elastic body, instead of like body forces. In the case of double surface layers, we have the further possibility that there may be forces of the nature of kinetic reactions due to bombardment by flying electrons. Such forces are certainly not like body forces in nature. Furthermore, the equilibrium argument demands an inexhaustible supply of freely movable electricity in the surface layer; we have no assurance that this electricity is present. In this paper my position is that it is not justifiable to put local impressed E.M.F.'s equal to local potential jumps. I shall use separate letters for these quantities and

THE VOLTA EFFECT.

The Volta effect next concerns us. There has been continuous discussion over this without yet any final agreement. There is, however, no question regarding the fundamental experimental facts. If two pieces of metal, say Cu and Zn, are brought into metallic contact, it is found that points in the surrounding medium, gas or vacuum, immediately outside the surfaces of the two metals, are at a difference of potential characteristic of the metals and the medium. When the medium is a perfect vacuum we define the potential as the true Volta potential difference. This difference may be measured in the regular way as the limit of the ratio of the work done on an electrostatic charge to the charge as the charge is made smaller.

The existence of a Volta potential difference follows as a matter of necessity if we suppose jumps of potential between the interior of Zn and ether, interior of Cu and ether, and between interior of Zn and Cu. The Volta jump Zn-Cu is the sum of the jumps ether-Zn, Zn-Cu, and Cu-ether. These jumps of potential demand the existence of corresponding double layers at the corresponding surfaces of separation. The precise strength of each double layer must remain conjectural as long as we have no method of determining the potential of points inside the metal. On the surfaces of Zn and Cu there is, in addition to the double layers, such a distribution of true electricity that under its action and that of the double layers, as computed by the law of the inverse first power, the space immediately outside the surface of each conductor is at constant potential, the potentials outside each conductor differing by the characteristic difference. If the geometrical configuration of Zn and Cu is changed, the single charges redistribute themselves on the surface so as to continue to satisfy the conditions. In particular, if Zn and Cu are made in the shape of plates, we may get the well known condenser action as their distance apart is varied.

The Volta potential difference is maintained automatically by some mechanism in the metal. A consequence of this is that if two pieces of Zn and Cu are charged out of contact with each other to a potential difference V (as measured between points in the surrounding ether immediately outside each metal), and are then brought into contact with a drop of potential difference to V_{zc} (where V_{zc} is the Volta difference), and passage of an amount of electricity E, the amount of electrical energy yielded by the system available to outside agencies is $E[(V - V_{zc})/2]$.

It may be shown by detailed analysis of any cyclic process involving the Volta effect that such a mechanism, automatically maintaining a

constant difference between the metals, does not involve a violation
the first law of thermodynamics.

Up to the present no way has been discovered of isolating the jumps
potential involved in the Volta effect. There have, however, been tw
principal points of view. One is that between points in different meta
on opposite sides of a surface of separation there is only a very sma
potential jump, numerically equal to the Peltier heat, and that th
characteristic jumps are located between the metal and the ether; whi
the other point of view is that there is no jump between metal an
ether, but that the entire Volta jump takes place between points wit
in the metals, on opposite sides of their surface of separation. In th
following I shall assume neither of these extreme positions, but sha
assume potential jumps and the corresponding double layers bot
between metal and ether and between metal and metal, subject to th
single restriction that the sum of the jumps gives the observed Vol
jump.

As already mentioned I shall not assume that there are impresse
E.M.F.'s at the surfaces equal and opposite to the potential jump
Neither shall I make the assumption, to me entirely unjustifiable, th
at the surface of separation of two metals here is an impressed E.M.
equal to the Peltier heat. Electricity must now be recognized as
substance capable of possessing kinetic and potential energy. Und
these conditions there is no necessary connection between merely th
heat and work absorbed when electricity passes from one locality
another.

The Thermo-Electric Circuit.

We are now in a position to discuss the ordinary thermo-electr
circuit. In order to have the entire situation immediately before us
will pay to reproduce the usual analysis. Consider a circuit of two met
A and B with junctions at t and $t + \Delta t$. The thermo-electric acti
shall be in such a direction that current flows from A to B at the h
junction. In practise the current usually attains such a value that t
energy input is all used in overcoming Ohmic resistance, but we migh
if we pleased, insert an electromagnetic engine in the circuit and obta
useful mechanical work. For the present we disregard the irreversib
aspects of this process, and assume that the circuit may be treated li
a perfect thermodynamic engine. The first law of thermodynam
states that in any closed cycle the energy input equals the energy outpu
We will take the closed cycle to be constituted by the flow around t
circuit of unit quantity of electricity; this extension of the idea of cy
is justified by the fact that after completion of the process every pa

of the system has returned to its original condition, and so there has been no change of internal energy. The energy output of the cycle is that which might be obtained from the current by an electro-magnetic engine, and for unit quantity of electricity is simply equal the E.M.F. of the circuit measured in appropriate units. We denote this E.M.F. by ΔE_0, where E_0 is the E.M.F. of the cycle between the fixed lower temperature t_0 and a variable upper temperature. The energy input of the cycle is heat input and occurs in four places: at the two junctions and in the two metals A and B. At the junction the reversible heat generated is called the Peltier heat. We denote by P_{AB} the heat absorbed by unit quantity of positive electricity in flowing from A to B. In a steady state, heat absorbed by the current is provided by an inflow of heat from the surroundings. In virtue of reversibility, $P_{AB} = -P_{BA}$. In the wires themselves there is also the reversible Thomson heat. We denote by σ_A the heat absorbed by unit quantity of positive electricity in flowing in the metal A from a lower temperature to a temperature 1 degree higher. σ corresponds to the "specific heat" of electricity. P_{AB}, σ_A, and σ_B are all functions of the temperature. It is a matter of experiment that σ does not depend on the temperature gradient.

There have been in the past numerous attempts to show that σ does depend on the temperature gradient, but the overwhelming concensus of opinion has been that all such supposed effects are to be explained by local inhomogeneities in the metal. Recently, however, Benedicks (3) has reopened the question, claiming to have established the existence of a legitimate effect. As far as his work on solids goes, a paper by Foote and Harrison (4) seems to me to fully meet the situation. With regard to liquid mercury I had, before knowing of Benedick's work, found negative results (5). I had shown that positive results will be obtained unless the apparatus is symmetrically located in the gravitational field. Benedicks does not mention any precaution of this nature, and I believe that his positive results are to be explained in this way. I shall assume in this paper that the effect does not exist.

The first law applied to the cycle now gives at once

$$\Delta E_0 = P_{AB}(t + \Delta t) - \sigma_B \Delta t - P_{AB} + \sigma_A \Delta t,$$

or

$$\frac{dE_0}{dt} = \sigma_A - \sigma_B + \frac{dP_{AB}}{dt}. \qquad (1)$$

In virtue of the experimental fact that the E.M.F. of a circuit from t_1 to t_2 plus that of one from t_2 to t_3 is equal that of a single one from t_1 to t_3, dE_0/dt is independent of t_0, and we write simply dE/dt, where the t_0 from which E is measured need not be specified, and in particular has

no relation to the temperature at which the σ_A, σ_B, and dP_{AB}/dt of the equation are taken.

The second law may also be applied, giving

$$\frac{P_{AB}(t+\Delta t)}{t+\Delta t} - \frac{\sigma_B \Delta t}{t+\Delta t/2} - \frac{P_{AB}}{t} + \frac{\sigma_A \Delta t}{t+\Delta t/2} = 0.$$

This may at once be rewritten in the form

$$\Delta\left(\frac{P_{AB}}{t}\right) + \frac{\sigma_A - \sigma_B}{t+\Delta t/2}\Delta t = 0,$$

and gives in the limit

$$\frac{d}{dt}\left(\frac{P_{AB}}{t}\right) + \frac{1}{t}(\sigma_A - \sigma_B) = 0. \qquad (2)$$

We may now eliminate $\sigma_A - \sigma_B$ or P_{AB} between 1 and 2, obtaining

$$P_{AB} = t\frac{dE_{AB}}{dt} \qquad (3)$$

$$\sigma_B - \sigma_A = t\frac{d^2E_{AB}}{dt^2}. \qquad (4)$$

In order to show that the E.M.F. is in such a direction that the curren flows from A to B at the hot junction, we write E with the subscript A and B.

Two aspects of these equations require discussion; first the irreversibl aspects of the process, and second the location of the E.M.F.

There are two irreversible processes always involved in any thermo electric circuit; generation of Joulean heat by the current in overcomin the resistance of the wire, and conduction of heat from the hotter to th colder end of the wire. In the early days of the subject it did not seem very objectionable to entirely disregard these effects, because of th probability that they were due to entirely unrelated parts of the mechan ism, so that it would be conceivable that a metal might exist with th same thermo-electric properties as any actual metal, but with negligibl thermal conduction and Joulean heat loss. But with the rise of electro theories of metals it became exceedingly probable that all these effects reversible and irreversible, are tied together by the same mechanism so that we cannot, at least without justification, assert that any aspect unimportant. It was this feeling which inspired Lorentz's article in th Wolfskehl conference collection. (6) Thomson also always regarded th thermodynamic argument as by itself unsatisfactory, and looked o the equations obtained by the method above merely as suggestive rel tions to be tested by experiment.

It is not unusual in elementary text books to find the statement tha

by properly choosing the dimensions of the circuit the irreversible aspects may be made vanishingly small. An argument by Boltzmann (7) in a much neglected paper shows, however, that this is not true, but that the ratio of irreversible to reversible heat can be reduced only to a minimum, not zero, by a proper choice of the constants of the circuit. Work is extracted from the circuit reversibly by an electro-magnetic engine of properly chosen back E.M.F. The dimensions of the parts of the circuit and the magnitude of the back E.M.F. are the only variables under our control. Suppose now that the best construction possible has been given to the circuit by a proper choice of all the independent variables. We may write down the thermodynamic inequalities that hold for an irreversible process, and obtain a necessary condition between the electrical and thermal conductivities and the thermo-electric constants. This condition is given by Boltzmann and is

$$t\frac{dE}{dt} - P \leqq 2A\sqrt{t}, \tag{5}$$

where

$$A = R_A^{1/2}K_A^{1/2} + R_B^{1/2}K_B^{1/2}$$

and R_A = specific electrical resistance of A,
K_A = specific thermal conductivity of A,

with corresponding letters with subscripts B for the corresponding properties of B.

The necessary condition written down above on the assumption that the reversible and irreversible aspects of the thermo-electric circuit are inextricably tied together to form one essentially irreversible process is not one which in practice imposes any useful restriction on the constants. $2A\sqrt{t}$ is in nearly every known case greater than $t\cdot dE/dt$ alone, which may always be made positive by a proper arrangement of the metals, and is thus necessarily greater than $t\cdot dE/dt - P$, because in every known case P is also positive when $t\cdot dE/dt$ is made positive. Experimentally, $t\cdot dE/dt$ is fairly easy to determine accurately, the difficulty being with P. So long, therefore, as $t\cdot dE/dt$ alone is less than $2A\sqrt{t}$, no amount of experimental inaccuracy would vitiate the inequality, which thereby loses all interest.

Many direct experimental attacks have been made on the question of the equality of $t\cdot dE/dt$ and P, but the experimental difficulties are great, and the experimental verification is still far from complete. Thus it was not until 1906 (8) that the reversibility of the Peltier heat was shown with any accuracy, the reversibility usually being assumed in experimental work and used as a means of eliminating the Joulean heat.

So far as I know, there is no evidence that $t \cdot dE/dt$ and P are not equ and with increasing accuracy of experimentation the verification becon closer. Gottstein (9) has published data on silicon, molybdenite graphite, in which the effects are large, and which other considerati suggest as the most likely field for discrepancies, and has obtai verification within the limits of accuracy of P, which are about 8 per ce Caswell (10) has also recently published data on several Bi Sn allo in which the effects are also large, and obtained verification withi per cent. He states that the accuracy of the Peltier heat measureme is 2 per cent., but also explicitly emphasizes that his measurements h proved the thermodynamic relation.

Mention should be made in this connection of a theorem of Baedel (11) to the effect that if the relation

$$\frac{dE_{AB}}{dt} = \frac{1}{t} P_{AB}$$

is true for a single pair of substances it is true for every pair. The pr given by Baedeker does not justify so general a statement as this, ho ever, and presumably the theorem itself does not hold. Baedeke proof is as follows. The relation (2) above becomes, if extended include irreversibility,

$$\frac{d}{dt}\left(\frac{P_{AB}}{t}\right) + \frac{1}{t}(\sigma_A - \sigma_B) \geq 0.$$

Combining this with equation 1 gives

$$\frac{dE_{AB}}{dt} \geqq \frac{1}{t} P_{AB}.$$

The equality sign holds for perfect reversibility. Suppose now that t equality sign holds for a special pair of metals, so that

$$\frac{dE_{AB}}{dt} = \frac{1}{t} P_{AB}.$$

Consider now the couples AC and CB, where C is any third met Because of the addition theorem we have

$$\frac{dE_{AC}}{dt} + \frac{dE_{CB}}{dt} = \frac{1}{t}(P_{AC} + P_{CB}).$$

Now if

$$\frac{dE_{AC}}{dt} > \frac{P_{AC}}{t},$$

we must evidently have

$$\frac{dE_{CB}}{dt} < \frac{P_{CB}}{t},$$

which, Baedeker says violates the second law, and hence the theorem. Baedeker failed to notice, however, that in the above inequality the metals must be arranged in such an order that dE_{AB}/dt is positive. His proof therefore holds only when dE_{AC}/dt and dE_{CB}/dt are both positive. The correct theorem is that if the relation of perfect reversibility holds for any pair of metals A and B (dE_{AB}/dt being positive), it also holds for all pairs of metals between A and B that may be chosen from the series of metals arranged in ascending order of dE_{Ax}/dt.

In practise, however, an equation can only be shown to hold within limits. So that instead of a perfect equality we should only have

$$\frac{dE_{AB}}{dt} = \frac{1}{t} P_{AB} + \epsilon,$$

where ϵ is some positive quantity. The argument above now shows that if C is any third metal intermediate between A and B, dE_{AC}/dt cannot exceed P_{AC}/t by more than ϵ. But dE_{AC}/dt is numerically less than dE_{AB}/dt, so that the percentage verification of the formula for the pair AC is not so good as for the pair AB.

If therefore a method is available in which the limits of accuracy are percentage limits, this theorem, contrary to what Baedeker supposed, does not allow us to dispense with an experimental verification of the formula for every pair of metals.

There is no inequality corresponding to

$$\frac{dE_{AB}}{dt} \geqq \frac{P_{AB}}{t}$$

connecting the Thomson heats with the electromotive force of the circuit. The analytical reason is that the two sides of an inequality may not be differentiated. The experimental verification of the formula for the Thomson heats is not yet as complete as that for the Peltier heat.

I shall assume in the following, as most probable from the present data, that the thermodynamic relations obtained by neglecting irreversibility are strictly true, but in my opinion the question cannot yet be regarded as closed.

Consider next the location of the E.M.F. A glance at the thermodynamic arguments shows that we have said nothing about the intensity of the forces at any locality; we have merely equated the total work done in the circuit by the E.M.F. to the total energy inflow in the form of heat, and our justification is the experimental fact that in the complete cycle no other forms of energy have any net effect. The thermodynamic results are entirely unaffected by adding to any possible physical dis-

around the complete circuit. Any argument for a localized E.M
must use other kinds of experimental fact than those which we h
up to the present used. There has, nevertheless, been an attempt
many physicists to identify the reversible heats with exactly e
E.M.F.'s at the same localities, and conversely. Maxwell does
as did also Heaviside (12), who speaks with impassioned irritation
those who would "make a force do work where it is not." All the ob
tions of Heaviside as to energy manifestations at the junctions seem
me to be fully answered by a careful consideration of the nature of
Poynting vector, together with a recognition of the fact that within
metal electricity may possess kinetic and potential energies characteri
of the metal. Whatever assumption one cares to make about the l
tion of the E.M.F. will be found to involve such a distribution of
Poynting vector as to automatically take care of any unusual ene
transformations introduced by the assumptions. However, in accordan
with the mode of thought of Maxwell and Heaviside it is usual to spe
of a Peltier E.M.F. and a Thomson E.M.F. (e.g., Caswell 1105, 1
which are precisely equal to the corresponding reversible heats, and
assume that these are the total E.M.F.'s at the junction or in the
equally heated metal. This, it seems to me, is entirely unjustified.
my position in this paper is that we know nothing about these local
E.M.F.'s from experiments such as these on closed circuits. When in
following I speak of a Peltier E.M.F., I mean whatever E.M.F., if a
there may be at the junction, but shall assume no relation with the h
at the junction. Similarly by the Thomson E.M.F. I mean the E.M
distributed throughout the metal in virtue of the temperature gradie
but again shall assume no relation with the Thomson heat.

A second point of view, that other specifiable E.M.F.'s than th
corresponding to the local heats are involved has been maintained
many. Among the prominent early holders of this view was L
Kelvin, who believed that at the junction of two metals there is an E.M
equal to the ordinary Volta contact potential difference. Adopting t
point of view, Kelvin in one of his later papers (13) deduced a relat
between Volta potential difference and a quantity analogous to
Peltier heat by a purely isothermal process, thus avoiding the difficul
of irreversibility. The same relation had also been given nine ye
previously by Lorentz (14) in a paper corrected by him to meet
criticisms of Budde (15). Both the papers of Kelvin and Lorentz se
to have been entirely overlooked by subsequent writers. It is n
becoming evident, however, from such work as that of Richardson

than the other, and that there may be a potential jump between the surface of the metal and the surrounding ether. I shall show from an examination of the phenomena of thermionic emission that there are certain relations between the E.M.F. of a circuit, Peltier heat, Volta potential difference, etc., irrespective of what hypothesis one adopts about the location of the potential jumps. Richardson himself makes the assumption that the local E.M.F. is equal the local heat, and with this assumption obtains a relation similar to Kelvin's.

Temperature Coefficient of Volta Effect.

The following deduction of a relation involving Peltier heat and Volta difference is considerably simpler than that of either Lorentz or Kelvin, and furthermore makes no assumptions as to the location and magnitude of the surface potential jumps accompanying the Volta potential difference. The method also permits somewhat more general conclusions.

Imagine an infinite plate condenser composed of two different metals A and B, all parts of which are maintained at the same temperature, and the distance apart of which is variable. The two plates may be connected by a wire. We imagine this wire to be half of A and half of B, so that when charge is transferred from one plate to the other through the wire the ordinary Peltier heat is developed at the junction.

As the independent variables fixing the state of the system we choose:

t = absolute temperature,
ρ = positive charge per unit area on A (there is of course an equal negative charge on B),
c = capacity per unit area (this depends only on the distance apart of the plates).

The following dependent variables are to be considered:

V_{BA} = Volta contact difference of potential,
u = internal energy per unit area,
dW = work done by the system in any infinitesimal change,
dQ = heat absorbed in any infinitesimal change.

Now the second law states that $(du+dW)/t$ is an exact differential for any reversible change. We accordingly have to find dW and du. For dW we have the equation

$$dW = \left(\frac{\partial W}{\partial T}\right)_{\rho c} dt + \left(\frac{\partial W}{\partial \rho}\right)_{tc} d\rho + \left(\frac{\partial W}{\partial c}\right)_{t\rho} dc.$$

The partial derivatives may be evaluated as follows. Obviously no work is done if the temperature of the system is changed, keeping the

distance of separation of the plates constant, if at the same time n charge is transferred from plate to plate. The analytic statement o this is

$$\left(\frac{\partial W}{\partial t}\right)_{\rho c} = 0.$$

Again, if work is obtained by letting current flow from plate to plate th effective driving force is the difference of potential minus the Volt difference. The work done during this passage of current may b extracted by a reversible electro-magnetic engine in the wire betwee the plates. This gives

$$\left(\frac{\partial W}{\partial \rho}\right)_{tc} = -\left(\frac{\rho}{c} - V_{BA}\right) d\rho.$$

This is independent of assumption as to the location of the Volta jump whether it is a surface affair between the metal and the surrounding electron gas, or between the two metals, or both. The conclusions ar therefore independent of special hypothesis. Finally, if the distance apart of the plates is changed, thus changing the capacity, but keeping temperature and charge constant, we have the mechanical work

$$\left(\frac{\partial W}{\partial c}\right)_{T\rho} dc = \frac{1}{2}\frac{\rho^2}{c^2} dc.$$

This is an immediate consequence of the familiar expression for th work of collecting an electrical distribution from infinite subdivision $\frac{1}{2}\rho \times$ pot. diff. ($= \frac{1}{2}(\rho^2/c)$ in this case).

We may also treat du as we have dW, writing

$$du = \left(\frac{\partial u}{\partial t}\right)_{\rho c} dt + \left(\frac{\partial u}{\partial \rho}\right)_{tc} d\rho + \left(\frac{\partial u}{\partial c}\right)_{t\rho} dc.$$

Substituting now above, we have

$$\frac{1}{t}\left\{\left(\frac{\partial u}{\partial t}\right)_{\rho c} dt + \left[-\frac{\rho}{c} + V_{BA} + \left(\frac{\partial u}{\partial \rho}\right)_{tk}\right] d\rho + \left[\frac{1}{2}\frac{\rho^2}{c^2} + \left(\frac{\partial u}{\partial c}\right)_{t\rho}\right] dc\right\}$$

is a perfect differential. This statement will give us three equations because of the three independent variables, instead of only one equation as in the examples of elementary thermodynamics, where we are concerned with only two independent variables.

In the first place, from the coefficients of dt and dc, we obtain

$$\frac{\partial}{\partial c}\left\{\frac{1}{t}\left(\frac{\partial u}{\partial t}\right)_{\rho c}\right\}_{t\rho} = \frac{\partial}{\partial t}\left\{\frac{1}{t}\left[\frac{1}{2}\frac{\rho^2}{c^2} + \left(\frac{\partial u}{\partial c}\right)_{t\rho}\right]\right\}_{c\rho},$$

whence

$$-\frac{1}{2}\frac{1}{t^2}\frac{\rho^2}{c^2} - \frac{1}{t^2}\left(\frac{\partial u}{\partial c}\right)_{t\rho} + \frac{1}{t}\left(\frac{\partial^2 u}{\partial c \partial t}\right) = \frac{1}{t}\left(\frac{\partial^2 u}{\partial c \partial t}\right)$$

giving

$$\left(\frac{\partial u}{\partial c}\right)_{t\rho} = -\frac{1}{2}\frac{\rho^2}{c^2}.$$

But we have already seen that

$$\left(\frac{\partial W}{\partial c}\right)_{t\rho} = \frac{1}{2}\frac{\rho^2}{c^2},$$

so that

$$\left(\frac{\partial Q}{\partial c}\right)_{t\rho} = 0. \tag{6}$$

Therefore no heat is absorbed when the plates are moved with respect to each other at constant temperature and charge. This states a fundamental assumption of electrostatics to the effect that charged bodies may be moved relatively to each other with no thermal effects.

Secondly, from the coefficients of $d\rho$ and dc we get

$$\frac{\partial}{\partial c}\left\{\frac{1}{t}\left[-\frac{\rho}{c} + V_{BA} + \left(\frac{\partial u}{\partial \rho}\right)_{tc}\right]\right\}_{t\rho} = \frac{\partial}{\partial \rho}\left\{\frac{1}{t}\left[\frac{1}{2}\frac{\rho^2}{c^2} + \left(\frac{\partial u}{\partial c}\right)_{t\rho}\right]\right\}_{ct},$$

which expands to

$$\frac{\rho}{c^2} + \left(\frac{\partial V_{BA}}{\partial c}\right)_{t\rho} + \left(\frac{\partial^2 u}{\partial \rho \partial c}\right)_t = \frac{\rho}{c^2} + \left(\frac{\partial^2 u}{\partial \rho \partial c}\right)_t,$$

or

$$\left(\frac{\partial V_{BA}}{\partial c}\right)_{t\rho} = 0, \tag{7}$$

which states that merely changing the distance between the plates does not change the Volta difference. We have not thereby proved that the Volta difference cannot depend on the distance apart of the plates; we have merely proved that such independence is a logical consequence of the statements that we made about the nature of the Volta effect.

Formulas 6 and 7 are not given by Kelvin or Lorentz.

Finally, we obtain from the coefficients of dt and $d\rho$,

$$\frac{\partial}{\partial \rho}\left\{\frac{1}{t}\left(\frac{\partial u}{\partial t}\right)_{\rho c}\right\}_{tc} = \frac{\partial}{\partial t}\left\{\frac{1}{t}\left[-\frac{\rho}{c} + V_{BA} + \left(\frac{\partial u}{\partial \rho}\right)_{tc}\right]\right\}_{\rho c}.$$

Expanding,

$$\frac{1}{t}\left(\frac{\partial^2 u}{\partial \rho \partial t}\right)_c = -\frac{1}{t^2}\left[-\frac{\rho}{c} + V_{BA} + \left(\frac{\partial u}{\partial \rho}\right)_{tc}\right] + \frac{1}{t}\left[\left(\frac{\partial V_{BA}}{\partial t}\right)_{\rho c} + \left(\frac{\partial^2 u}{\partial t \partial \rho}\right)_c\right].$$

$(\partial^2 u/\partial \rho \partial t)_c$ cancels. $(\partial V_{BA}/\partial t)_{\rho c}$ we may take as the ordinary temperature derivative of the Volta contact difference of potential. Experimentally there is yet no evidence for a variation of V with ρ, and we have

dV_{BA}/dt, but the thermodynamic distinction between the derivat should not be forgotten. It might be proved experimentally at s later time that V_{BA} does depend on ρ, and in fact there are some plau reasons for expecting an effect of this nature. I am not aware that very careful search has been made for a variation of V with ρ.

The only unknown now remaining in the above equation is ∂u Under all conditions we have $du = dQ - dW$. Now if the temper is constant, and the distance apart of the plates is constant stant), the only mechanical work is that which might be got out of electrical current when ρ changes, and the heat absorbed is the involved in the transfer of electricity from one plate to the other. this for the moment as P_{BA}', this being the heat absorbed when quantity of electricity passes from B to A. Then

$$\left(\frac{\partial u}{\partial \rho}\right)_{tc} d\rho = P_{BA}' d\rho + \left(\frac{\rho}{c} - V_{BA}\right) d\rho.$$

Substitute this above and we get

$$0 = -\frac{P_{BA}'}{t} + \frac{dV_{BA}}{dt},$$

or

$$\frac{dV_{AB}}{dt} = \frac{P_{AB}'}{t}.$$

This is the equation deduced by Lorentz (14) and Kelvin (13). It be noticed that all parts of the system have been at the same tem ture, so that during the cycle there have been no irreversible heat t fers, and therefore there is no question of the validity of the conclu as there was in the case of the ordinary thermoelectric circuit. K hoped that an experimental confirmation of this formula would make probable the correctness of the ordinary formulas for the thermo el circuit. In attempting the confirmation he at first identified, a naturally would, the heat P_{BA}' with the ordinary Peltier heat This amounts to assuming that all the thermal effects involved i transfer of charge from B to A are to be found at the surface of sepa of A and B. Making this identification of P' with P, the experim verification failed by a thousand fold. Now the ordinary th dynamic formulas hold within much narrower limits. So that not did this attempt of Kelvin's to place the ordinary thermodyn ing on a firmer basis fail, but in order to explain the discrepa the new formula and experiment, he was driven to postula e of another surface thermal effect, in much the same way reviously postulated the existence of the Thomson heat.

possibility of such a surface heat was also explicitly recognized by Lorentz (14), after it was suggested to him by Budde (15).

The new surface heat that Kelvin had to postulate was a reversible generation or absorption of heat at the surface of a conductor when the surface charge changes. So far as I am aware the existence of the effect has never been demonstrated; in fact the papers of Lorentz and Kelvin seem not to be generally known, and apparently no serious attempt has been made to discover the effect. I shall return to this matter later in connection with a deduction of the same formula by a method similar to that of Richardson.

THERMIONIC EFFECTS.

This is probably as far as we can get by an application of the two laws of thermodynamics to these two phenomena. Further progress demands different types of experiments from those contemplated in the applications above. Now this new order of experimental fact has been supplied in the last few years, in principal part by the work of Richardson (16) on thermionic emission. In this work the energy relations and transformations are discussed when electricity is taken directly through the surface of the metal from metal to ether. In the previous work of this paper we have been restricted in transferring electricity from conductor to conductor to the staid and classical methods of motion over the metallic surfaces or through the body of the metal. We may now extend our thermodynamic processes to cycles in which electricity is transferred from one conductor to another through the surface and the surrounding ether.

Richardson has developed by thermodynamic arguments many of the formulas connecting thermionic effects with those already discussed, but he has frequently made specific assumptions as to localized E.M.F.'s, and has further, it seems to me, confused or used interchangeably the thermodynamic quantities, quantity of energy, quantity of heat, and work, and has not sharply specified the conditions to which some of his quantities, notably the heat of vaporization of an electron, apply. A critical examination of his methods will suggest changes in his formulas.

The starting point is the observation that at high temperatures all metals emit electrons, and therefore, when in a state of equilibrium, are surrounded by an electron atmosphere. The density of this atmosphere becomes rapidly lower at lower temperatures, but we assume that it essentially exists at all temperatures, and obtain what information we can from the fact of its existence. The density of this gas is so small under ordinary conditions that the charge it carries does not affect its

given a qualitative argument for this, or it may be easily proved by writing down the equations of equilibrium of a gas in which there is a distributed volume charge proportional to the density, and finding the explicit solution for small densities.

The process of a metal surrounding itself with an electron atmosphere is analogous to the process of evaporation of a solid, and the same thermodynamic arguments apply to it. Any purely electrostatic action due to the isolation of the negative charge in the gas and a positive charge on the metal can be eliminated by evaporating only a small quantity of electrons, the electrostatic energy being proportional to the square of the charge. Assuming now the perfect gas law, we first find the relation between electron gas density and temperature.

Clapeyron's equation applies to this and gives

$$\frac{dt}{dp} = \frac{t\Delta v}{H},$$

where Δv is the change of volume when 1 gm. of electrons evaporates reversibly, and H is the latent heat of evaporation. Professor Hall has objected to the use of this equation, or the equivalent one by Richardson (Eq. 1, p. 28 of Richardson's book), and has published a statement to that effect in a recent number of the Proceedings of the National Academy of Sciences (17). He has later recognized, however, that the objection to Richardson's argument is not to be found at this stage, and is stating his revised position in a forthcoming note to the National Academy.

Returning now to Clapeyron's equation, since the perfect gas law holds, $p = nkt$, where n is the number of electrons per c.c., and k is the gas constant. The gas law now gives

$$dp = ktdn + nkdt.$$

Δv is obviously approximately equal to v, the volume of 1 gm. of electron gas. Making these two substitutions in Clapeyron's equation, we get

$$dt = \frac{tv}{H}(ktdn + nkdt),$$

which may be rewritten

$$dt = \frac{kt^2}{\frac{H}{nv}}\left(\frac{dn}{n} + \frac{dt}{t}\right).$$

Now nv is the total number of electrons per gm. of gas, and hence H/nv is the latent heat per electron. Denote this by η, and the equation becomes

$$\frac{\eta dt}{kt^2} = \frac{dn}{n} + \frac{dt}{t}. \qquad (9)$$

An integration of this equation gives

$$n = At^{-1}e^{\int \frac{\eta dt}{kt^2}}, \tag{10}$$

in which A is not a function of t. This is the same as Richardson's equation 7, p. 29, noting that his φ is the energy change in the evaporation of one electron, so that $\eta = \varphi + kt$.

It is necessary to scrutinize pretty closely the conditions under which the η of this formula is to be determined. Clapeyron's equation, as used above, applies to an isolated system of metal with its electron vapor. We may imagine this system enclosed in a box provided with a piston working on the electron vapor, and so able to interchange work with the surroundings. The η in the formula above is the heat per electron which must be communicated to the box from outside during the evaporation of electrons and accompanying motion of the piston at constant pressure. Now during this process in which an electron is evaporated, a positive charge is left behind on the surface of the metal, so that during this process the surface charge is changing. We may split η into two parts. The first, η_ρ, is the latent heat which would be absorbed if the evaporation took place at constant surface charge. The second part of the heat is a heating effect due to the appearance of a positive charge on the surface; this is merely Lorentz and Kelvin's surface heat. If we put P_s for the heat absorbed by the system when unit positive charge is imparted to the surface, we have

$$\eta = \eta_\rho - \epsilon P_S, \tag{11}$$

where ϵ is the electronic charge, taken as a negative number.

These results may now be applied to contact difference of potential. Imagine two metals A and B together in a region at temperature t, in metallic contact. Each metal will sourround itself with an atmosphere of electrons by spontaneous emission, and these two atmospheres will in general be of different densities and pressures. The gas equilibrium is maintained by an electrostatic potential gradient accompanying the pressure gradient. Notice that this equilibrating electrostatic field, for gases of small densities, is due to charges outside the gas itself. The ordinary gas equations show that equilibrium demands the equation

$$\frac{n_A}{n_B} = e^{-\frac{\epsilon v}{kt}BA}, \tag{12}$$

where ϵV_{BA} is the work done against electrostatic forces in taking an electron from a point immediately outside B to a point immediately outside A, n_A and n_B are the number of electrons per c.c. immediately outside A and B respectively.

Under ordinary conditions it is doubtful whether two pieces of m
ever reach equilibrium in this way, because the emission of electron
ordinary temperatures is so excessively slow. From data on page 76
Richardson it may be computed that a sphere of tung ten 1 cm in ra
requires something of the order of 10^{65} years to charge itself to a poten
of 1 volt by spontaneous emission of electrons at 0° C. It is to be
sidered, therefore, whether the Volta potential difference as measu
under ordinary conditions is the same as it would be if measured
a time long enough for the attainment of equilibrium conditions. N
it is reasonable to suppose that the potential jumps at the surfac
metal and ether or metal and metal are determined solely by for
operative at the surfaces, little if any affected by the presence of
electron gas outside. In a system of two metals in contact there
be jumps of potential at four places; at the three surfaces of separat
of metal-ether or metal-metal, and through the ether between po
outside the two metals. The sum of the four drops is zero, because
electrostatic field is conservative. Three of the drops are the s
probably, whether equilibrium is reached or not. The fourth dr
which is the Volta drop, is therefore also probably the same whet
equilibrium is reached or not. We may therefore apply our ther
dynamic reasoning to systems in which equilibrium has been attai
with high probability that the Volta drop appearing in the formula
the same as that measured under ordinary conditions.

We are now in a position to obtain V. Taking logarithms of
equation (12) above,

$$V_{BA} = \frac{kt}{\epsilon} \log \frac{n_B}{n_A}.$$

Substituting values of n

$$V_{BA} = \frac{kt}{\epsilon} \left\{ \log \frac{A_B}{A_A} + \int \frac{\eta_B - \eta_A}{kt^2} dt \right\}.$$

Now A_A and A_B are independent of t. Hence, differentiating the abo
equation,

$$\eta_A - \eta_B = \epsilon V_{BA} - \epsilon t \frac{dV_{BA}}{dt}.$$

It is to be noticed that during this differentiation all the other variab
on which the quantities might conceivably depend are to be kept c
stant. In particular, if V_{BA} is possibly a function of the total charge
the surface, we should have to keep the surface density constant dur
the differentiation, and dV_{BA}/dt would become $(\partial V_{BA}/\partial t)_\sigma$, as in
previous deduction by the condenser method.

We may obtain another relation by taking a gram of electrons around a closed cycle between A and B. This cycle may be performed in the following way. Imagine separate enclosures about A and B, containing the electron gas, and connected by a pipe in which there is a piston (see Fig. 2). The piston is to be pushed toward the enclosure about B and withdrawn by the corresponding amount from that about A. This transfers electrons from the gas about B to the gas about A. During the process of transfer of electrons from the atmosphere about B, through the metal, to the atmosphere about A, there has obviously been no change in the surface charges on A or B. The latent heats of vaporization

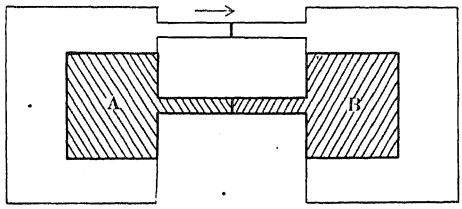


Fig. 2.

involved in this process will therefore be the heats at constant charge. Now the process outlined above is isothermal and reversible, and therefore the total heat absorbed is zero. This gives

$$\eta_{\rho A} - \eta_{\rho B} + \epsilon P_{BA} + Q = 0.$$

P_{BA} is the ordinary Peltier heat at the junction. Q is the heat absorbed by the gas per electron in passing under equilibrium conditions from the gas about A to that about B. In this transfer the gas remains isothermal, and pressure and potential change simultaneously as equilibrium demands.

Now the analysis of the introduction shows that when a gas is displaced in this way in a potential field the mechanical work done by the pressures acting across the boundaries is zero. The first law of thermodynamics demands, therefore, that the heat inflow shall equal the change of energy. This change is composed of two parts, energy of position in the field, and intrinsic energy. But now the intrinsic energy of a gas does not change at constant temperature. Hence

$$Q = \epsilon V_{AB}.$$

We may apply our definition of E.M.F. given in the introduction and find the E.M.F. between two points in the electron gas outside A and B to be V_{AB}. In this particular case, therefore, electrostatic potential difference, local E.M.F., and heat locally absorbed are numerically equal.

The reason is that in this particular case (electron gas) the intr
energy of the electrons is a function of temperature only. We
prove later that this equality cannot hold in general.

The Q found as above is the same as that which would be found
the ordinary formulas for a substance not in a field of force.
calculation gives

$$Q = \int_{p_A}^{p_B} \left(\frac{\partial Q}{\partial p}\right)_t dp = -\int_{p_A}^{p_B} t\left(\frac{\partial v}{\partial t}\right)_p dp.$$

For a perfect gas this becomes

$$Q = -kt\int_{p_A}^{p_B}\frac{dp}{p} = kt\log\frac{p_A}{p_B} = kt\log\frac{n_A}{n_B}.$$

But we have seen that the condition of equilibrium in a potential fi

$$\log\frac{n_A}{n_B} = -\frac{\epsilon V_{BA}}{kt}.$$

Substituting,

$$Q = \epsilon V_{AB},$$

as before.

We would not be justified, however, in assuming that the
formulas of thermodynamics are not affected by the presence o
potential field. In particular, the work done by a gas in expa
isothermally against the pressures exerted across its boundaries
when there is no potential field. We have just seen that this w
zero in a potential field. Work in a potential field is therefore not
to $\int pdv$.

Instead of saying as above that the heat absorbed goes directly t
increasing the energy of position, we may, if we prefer, descri
phenomena by saying that the heat absorbed goes to the work
would normally be done by the gas in expanding out of a potential
and that besides this work, additional work is received across the
daries when expanding in a potential field, which goes to increa
energy of position.

Now substituting the value found for Q gives

$$\eta_{\rho A} - \eta_{\rho B} = \epsilon(V_{BA} - P_{BA}).$$

An equation similar in appearance was given by Richardson, in
$\eta_{\rho A} - \eta_{\rho B}$ is replaced by $\varphi_A - \varphi_B$. He obtained the equatio
identifying φ_A, φ_B and P_{AB} with the local E.M.F.'s, and by disreg
the difference between the heats of vaporization at constant s
density and with variable density.

In a recent paper, Langmuir (18), essentially following Richar

point of view, has also failed to recognize the difference between the heat of vaporization at variable surface density, which appears in the thermodynamic analysis, and the heat under constant surface density, which may be measured experimentally. Langmuir's calculation of the magnitude of the heat of vaporization from the work done by an electron in escaping from the attraction of its image in the surface applies to vaporization with variable surface density, and not to the experimental conditions of vaporization at constant density. His argument for the probable non-existence of the double layer on the surface metal-ether would therefore seem to me to lose much of its force. This failure to distinguish between the two heats of vaporization would also seem to be involved in Langmuir's formulation (on page 172 of his paper) of the distinction between a potential difference and an E.M.F.

Combining the two equations (13), and (14), for $\eta_{\rho A} - \eta\rho_{\rho B}$, with (11) gives,

$$t\frac{dV_{BA}}{dt} = P_{BA} + P_{AS} - P_{BS}. \qquad (15)$$

Now if positive charge is passed from the surface of B to A through the metal, as in the condenser analysis previously given, negative charge appears on B and positive on A, and there may be accompanying heating effects in three places, at the two surfaces of separation of metal from ether, and at the surface metal-metal. The sum of these three heats is what was previously called P_{BA}'. Obviously

$$P_{BA}' = P_{BA} + P_{AS} - P_{BS}, \qquad (16)$$

and we have

$$t\frac{dV_{BA}}{dt} = P_{BA}', \qquad (17)$$

which is the equation (8) of Lorentz and Kelvin previously given. As already stated, it would be more correct, until more definite experimental evidence is at hand to write $\partial V_{BA}/\partial t$ instead of dV_{BA}/dt.

The deduction of this same equation by methods so different is pretty good presumptive evidence of its correctness.

The equation corresponding to the above given by Richardson is

$$t\frac{dV_{BA}}{dt} = P_{BA},$$

where P_{BA} is the ordinary Peltier heat. The surface heats do not appear in his equation, because, as already explained, he has neglected to distinguish latent at heats at constant from those at variable surface charge.

Assuming Richardson's formula to be correct, we may combine with

the formulas for a thermo-electric circuit, obtaining the relation

$$\frac{dV_{AB}}{dt} = \frac{dE_{AB}}{dt}.$$

This consequence of Richardson's relation is frequently supposed to be correct,[1] but obviously is not correct if there is a surface heat.

The formula above as given by Richardson has never been verified experimentally. The failure of experimental verification may very well be due in large part to experimental difficulties. Recent work of Langmuir (19) has shown the enormous effect on a metal surface of a layer of adsorbed gas only one molecule deep. No experiments on this subject have ever been made in which this layer has been removed. Perhaps the most recent work is that of Compton (20), in which there is a large possible effect from residual gas, as he himself explicitly states. The experimental discrepancy has been reduced by this latest work of Compton from the thousand fold of Kelvin to fifty fold. There is still, however, as far as the best experimental evidence goes, ample room for the existence of the surface heat.

In view of the important rôle which the equation of Richardson plays in the subject of thermionic emission, the question of the existence of the surface heat assumes considerable interest. A direct experimental attack on the problem does not appear promising. Assuming in the most favorable case that the entire outstanding discrepancy in the formula

$$t\frac{dV_{BA}}{dt} = P_{BA}$$

is due to the hypothetical surface heats, the rise of temperature of a conductor on imparting to it a surface charge may be computed approximately. The greatest rise of temperature will be produced on thin conductors, such as wires or foil. But under these conditions the greatest effect to be expected is entirely overwhelmed by the heating effect due to the mechanical stress produced in the conductor by the mutual repulsion of the charges on the surface. (It is to be remarked that the above does not include this electrostriction effect, which may be made vanishingly small by working with large enough conductors.) The best chance of detecting the existence of the surface heat is by an experimental determination of dV_{BA}/dt, improving the vacuum conditions as much as possible, or by a method to be suggested later.

Professor Hall in a recent paper (17) has stated his belief in the existence of the surface heats. He argues for their existence by giving such a picture of the mechanism involved in a redistribution of surface charge

[1] See, for example, Langmuir, *loc. cit.*, page 182.

as to make a heating effect seem probable. His conception is that at every point within and on the surface of a metal there is a dissociation of atoms into positive and negative ions, whose relative number is determined by the mass law. A disturbance of equilibrium by the removal of electrons from the surface layer is followed by such a change in the surface dissociation as to again satisfy the mass law. This new dissociation, it is most natural to suppose, is accompanied by heating effects.

The introduction of the idea of a dissociation determined by the mass law is, I believe, a valuable addition to our stock of concepts of what may be taking place within a metal, and its application to the surface effects is one way of avoiding one very real difficulty. This difficulty is encountered in trying to picture the processes involved in giving a metal surface a positive charge. Let us suppose the surface initially uncharged, without surface layers. Then the surface may be given a negative charge by the mere addition of electrons, but to produce a positive charge, electrons must be removed from the interior of the atoms. These two processes are essentially different in character, and the last must almost of necessity involve a heating effect, which the first need not. There is thus a dissymmetry in the action of a positive and a negative charge which we are not willing to admit. The assumption of a continual supply of positive and negative ions in the surface, as Professor Hall suggests, avoids this dissymmetry, and to that extent has intrinsic probability. Nevertheless the extension of the concept of mass action to a surface layer seems questionable, and I believe the difficulty can be met in another way. If we suppose the surface is covered with a double layer, the electrons being on the side away from the metal, then a negative charge is added by adding electrons to the outer layer, and a positive charge is added by removing electrons from the outer layer. There is thus no difficulty from dissymmetry. I prefer, therefore, to regard the question of the existence of this surface heat as still open, to be settled by new experimental evidence, but incline to the opinion that it does exist.

We may now combine these thermionic formulas with those of the thermo-electric circuit. We introduce the following new quantities in addition to those already considered.

S_{AE} = potential jump at surface of separation of A and ether,
S_{BE} = potential jump at surface of separation of B and ether,
S_{AB} = potential jump at surface of separation of A and B,
Σ_{AE} = E.M.F. at surface of separation of A and ether,
Σ_{BE} = E.M.F. at surface of separation of B and ether,
Σ_{AB} = E.M.F. at surface of separation of A and B,
σ_A' = Thomson E.M.F. in A,

σ_B' = Thomson E.M.F. in B,
σ_A'' = Thomson potential gradient in A,
σ_B'' = Thomson potential gradient in B.

It may of course be questionable whether there is any E.M.F. at surface of separation of A and ether, and it is any event exceedin improbable that the surface action can be completely represented by E.M.F. It may be, however, that part of the action is properly representable. We denote this part of the action by the letters ab and find what conditions it has to satisfy.

With regard to the Thomson potential gradient it is to be emphas that this is entirely different in character from the surface jumps or S_{AB}. A jump of the potential at the surface necessarily involv double layer at the surface; the jump is entirely determined by double layer, and is unaffected by charges elsewhere. The surface ju is therefore probably determined by forces at the surface, which probably characteristic of the surface and independent of the stat other parts of the system. The Thomson potential gradient i.e., potential gradient in an unequally heated metal) is, however, affe by the distribution of charge throughout the system, and can there be characteristic of the system only under specified conditions. We s in the following understand by σ'' the potential gradient in open cir The Thomson E.M.F. and Thomson heat are, on the other hand, p ably determined merely by the local forces, independently of other p of the system. We shall assume then to be of this character in following.

We now have the following equations;

$$V_{BA} = \frac{1}{\epsilon}(\eta_{pA} - \eta_{pB}) + P_{BA},$$

$$V_{BA} = S_{AE} - S_{BE} + S_{BA},$$

$$V_{BA} = \Sigma_{AE} - \Sigma_{BE} + \Sigma_{BA}.$$

These three depend on the fact, already proved, that in the electron potential difference, E.M.F., and heat are locally equal. These t equations are obtained from the isothermal system by describin closed path out of the ether into B, across the surface of separa of B and A, out into the starting point in the ether. By describin closed path entirely within the metal, maintaining now the junction A and B at different temperatures, we may obtain the following t additional equations

$$\frac{dE_{BA}}{dt} = \frac{d\Sigma_{BA}}{dt} + \sigma_B' - \sigma_A', \tag{21}$$

$$\frac{dE_{BA}}{dt} = \frac{dP_{BA}}{dt} + \sigma_B - \sigma_A, \tag{22}$$

$$\frac{dE_{BA}}{dt} = \frac{dS_{BA}}{dt} + \sigma_B'' - \sigma_A''. \tag{23}$$

The last of these is the expression for the difference of potential between the ends of A and B on open circuit, assuming that the E.M.F. of a thermo-electric circuit is the same on open and closed circuit. This is matter for experimental examination; I do not know how carefully this examination has been made. Certainly the equality of E.M.F. on open and closed circuit is usually assumed without question, and in the absence of experimental evidence to the contrary, we shall make the same assumption here.

We also have the additional equations

$$\frac{P_{BA}}{t} = \frac{dE_{BA}}{dt} = \frac{dV_{BA}}{dt} - \frac{1}{t}[P_{AS} - P_{BS}]. \tag{24}$$

Now differentiating (18) and combining with (22) and (24) gives

$$\frac{d\eta_{\rho A}}{dt} + \epsilon\sigma_A - \frac{\epsilon}{t}P_{AS} = \frac{d\eta_{\rho B}}{dt} + \epsilon\sigma_B - \frac{\epsilon}{t}P_{BS}. \tag{25}$$

Similarly (20), (21), and (24) give

$$\frac{d\Sigma_{AE}}{dt} + \sigma_A' - \frac{P_{AS}}{t} = \frac{d\Sigma_{BE}}{dt} + \sigma_B' - \frac{P_{BS}}{t}, \tag{26}$$

and (19), (23), and (24) give

$$\frac{dS_{AE}}{dt} + \sigma_A'' - \frac{P_{AS}}{t} = \frac{dS_{BE}}{dt} + \sigma_B'' - \frac{P_{BS}}{t}. \tag{27}$$

Hence we have proved that

$$\frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{\epsilon P_S}{t}, \qquad \frac{d\Sigma_E}{dt} + \sigma' - \frac{P_S}{t}, \qquad \text{and} \qquad \frac{dS_E}{t} + \sigma'' - \frac{P_S}{t}$$

are all independent of the metal.

We may now obtain the universal value of $d\eta_\rho/dt + \epsilon\sigma - \epsilon P_S/t$ by an argument similar to that of Richardson. In this deduction we shall assume that the irreversible processes going on at the same time that we describe the various cycles are without effect.

Surround the two ends of the bar at difference of temperature by two chambers to contain the electron atmosphere (see Fig. 3), with pistons as shown. Electrons are first to be conveyed from one chamber to the

other by operating the pistons as shown. The cycle then is to be co
pleted in two steps. First, operate on the transferred gas under poten
$V + \Delta V$, allowing it to expand to temperature t and to that pressu
$p + \Delta p'$, which is in equilibrium at t with gas at pressure p at a poten
V. The second step consists in the transfer of gas at t from V
and $p + \Delta p'$ to V and p. During this second step V and p shall cha
together in such a way that they always have the simultaneous val
to be found in an isothermal gas in equilibrium extending from p, V

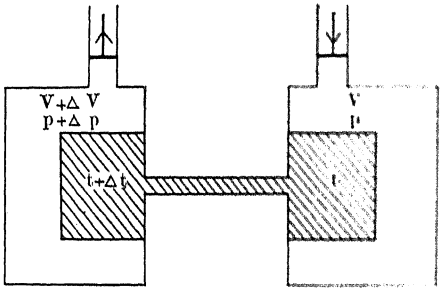


Fig. 3.

$p + \Delta p'$, $V + \Delta V$. To the first of these two steps all the ordinary
rmulas of thermodynamics apply, because the process is described
constant potential. During the second process, however, the poten
is changing, and all of the ordinary formulas do not apply. In p
ticular, we have shown that the work cannot be computed in the regu
way, but is zero. We have, however, shown that the heat absorbed,
therefore the change of entropy, is not affected by the fact that
process is described in a varying potential field. The change of entr
may therefore be computed for these two steps together in the regu
way, and therefore is independent of the precise way of passing fr
the initial to the final state.

Applying the second law to the cycle now gives

$$\frac{1}{\epsilon}\frac{\eta_p}{t} + \frac{\sigma \Delta t}{t + \frac{\Delta t}{2}} + \frac{1}{\epsilon}\frac{\eta_p + \Delta t \frac{d\eta_p}{dt}}{t + \Delta t} + \frac{1}{\epsilon}\int d\psi = 0,$$

where $\int d\psi$ is the change of entropy of the gas per electron on be
carried from $(t + \Delta t,\ p + \Delta p)$ to $(t,\ p)$, and may be computed by
ordinary thermodynamic formulas. Now

$$d\psi = \left(\frac{\partial \psi}{\partial t}\right)_p dt + \left(\frac{\partial \psi}{\partial p}\right)_t dp = \frac{C_p}{t} dt - \left(\frac{\partial v}{\partial t}\right)_p dp.$$

For a perfect gas, satisfying the equation $pv = kt$,

$$\left(\frac{\partial v}{\partial t}\right)_p = \frac{k}{p},$$

and

$$C_p = \frac{k\gamma}{\gamma - 1},$$

where γ is the ratio of C_p to C_v. Hence

$$\int d\psi = \frac{k\gamma}{\gamma - 1}\int \frac{dt}{t} - k\int \frac{dp}{p}.$$

Substituting in the equation above and taking the limit,

$$\frac{1}{\epsilon}\frac{d}{dt}\left(\frac{\eta_\rho}{t}\right) + \frac{\sigma}{t} - \frac{1}{\epsilon}\cdot\frac{k\gamma}{\gamma - 1}\cdot\frac{1}{t} + \frac{1}{\epsilon}\cdot\frac{k}{p}\cdot\frac{dp}{dt} = 0.$$

But we have already found that

$$\frac{1}{p}\frac{dp}{dt} = \frac{\eta}{kt^2} = \frac{\eta_\rho - \epsilon P_S}{kt^2}.$$

Hence the desired relation

$$\frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{\epsilon P_S}{t} = \frac{k\gamma}{\gamma - 1}. \qquad (28)$$

Instead of this equation Richardson gives

$$\frac{d\varphi}{dt} + \epsilon\sigma = \frac{k}{\gamma - 1}.$$

It differs from that deduced above in the absence of the surface heat. Richardson uses the value of φ as given by this equation to get the thermionic current. His formula checks with experiment, but is of such a form that only very wide changes in the form of φ could be detected. Thus, using the value he gives for φ, there is a factor t^2 in the value of current (formula 17, page 33), but he states later that equally good agreement is obtained if a factor $t^{1/2}$ replaces t^2. Richardson's data do not, therefore, afford a check on his value for φ. The neglect of the surface heat in Richardson's equation would therefore seem to be indefensible, and until the order of the effect is known, we cannot tell whether Richardson's equation is even approximately correct. It is to be noticed that Richardson's formula would become the same as that developed above in case P_S should be proportional to t. The φ of his formula must then be understood to be the change of energy on evaporation at constant surface charge.

We may now obtain further information by applying the first law to

the cycle, writing total work done in the complete cycle equal to absorbed. Work is done in the cycle when the piston is pushed into right hand chamber, when it is pulled out from the left hand chamber and when the gas expands in the first of the two processes mentioned above, but no work is done in the second of the two steps. Heat absorbed in all of the operations. The first law gives

$$\frac{d}{dt}(pv)\Delta t + \int_{t+\Delta t}^{t}\left(\frac{\partial W}{\partial t}\right)_p dt + \int_{p+\Delta p}^{p+\Delta p'}\left(\frac{\partial W}{\partial p}\right)_t dp$$

$$= \frac{d\eta_\rho}{dt}\Delta t + \epsilon\sigma\Delta t + \int_{t+\Delta t}^{t}\left(\frac{\partial Q}{\partial t}\right)_p dt + \int_{p+\Delta p}^{p+\Delta p'}\left(\frac{\partial Q}{\partial p}\right)_t dp \quad (\Delta$$

where

$$\int_{t+\Delta t}^{t}\left(\frac{\partial W}{\partial t}\right)_p dt = \int_{p+\Delta p}^{t} p\left(\frac{\partial v}{\partial t}\right)_p dt \quad k\Delta t,$$

$$\int_{p+\Delta p}^{p+\Delta p'}\left(\frac{\partial W}{\partial p}\right)_t dp = \int_{p+\Delta p}^{p+\Delta p'} p\left(\frac{\partial v}{\partial p}\right)_t dp \quad \Delta p \quad \Delta p'$$

$$\int_{t+\Delta t}^{t}\left(\frac{\partial Q}{\partial t}\right)_p dt = \int_{t+\Delta t}^{t} c_p dt = \frac{-k\gamma}{\gamma - 1}\Delta t,$$

$$\int_{p+\Delta p}^{p+\Delta p'}\left(\frac{\partial Q}{\partial p}\right)_t dp = -\int_{p+\Delta p}^{p+\Delta p'} t\left(\frac{\partial v}{\partial t}\right)_p dp \quad \Delta p \quad \Delta p'$$

Substituting these values, the left-hand side cancels out, leaving,

$$0 = \frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{k\gamma}{\gamma - 1} = \epsilon\frac{dV}{dt}.$$

But we found that

$$\frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{k\gamma}{\gamma - 1} = \frac{\epsilon P_s}{t}.$$

Substituting,

$$\frac{dV}{dt} = \frac{P_s}{t}. \quad (20)$$

This equation was also obtained by Lorentz (14) by an entirely different method.

Now dV/dt is the Volta difference per degree between different parts of the same unequally heated metal, provided that free circulation of the electrons from hot to cold through the electron gas is prevented. This is the Volta difference which would be observed at temperatures so low that the emission of electrons is negligible. We have here, therefore, a possible experimental method of detecting the existence of the surface heat P.

At temperatures so high that electron emission is not negligible there is no reason to expect that the free electron vapor is in equilibrium with

an unequally heated metal, but there is a possibility that electricity may flow in closed circuits, as shown in Fig. 4, through the electron gas and the metal. I am not aware that the existence of such currents has been detected or suggested. If it should happen that such currents do not exist, we may obtain an additional relation. The electrons spontaneously emitted by different parts of the surface must in this case be of such densities as to be in equilibrium under the potential gradient given by $dV/dt = P_S/t$. This gives, together with (9),

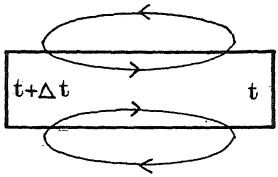


Fig. 4.

$$\frac{\eta}{kt^2} = -\frac{\epsilon}{kt}\frac{dV}{dt},$$

or

$$\eta_\rho - \epsilon P_S = -\epsilon P_S,$$

or

$$\eta_\rho = 0.$$

Now this condition is almost certainly not satisfied, so that it is exceedingly probable that closed circuits like those indicated do exist in an unequally heated metal.

Having found the value of dV/dt, we may now find the universal value of $d\Sigma_E/dt + \sigma' - P_S/t$ and $dS_E/dt + \sigma'' - P_S/t$. We may obtain the latter immediately by noting that the total change of potential in a closed circuit is zero. This gives

$$\frac{dS_E}{dt} + \sigma'' - \frac{dV}{dt} = 0.$$

Substituting for dV/dt,

$$\frac{dS_E}{dt} + \sigma'' - \frac{P_S}{t} = 0, \tag{30}$$

the desired relation.

Next to obtain the value of $d\Sigma_E/dt + \sigma' - P_S/t$, we may write down the expression for the total E.M.F. encountered in going from the electron gas surrounding the metal at t, through the metal, to the electron gas at $t + \Delta t$. Our definition of E.M.F. is total change of energy plus work delivered to outside agencies. The change of energy of the electron gas is an intrinsic change ($= k\Delta t$) plus the change of electrostatic energy ($= \epsilon\Delta V$). The work delivered is $d/dt \cdot (pv)\Delta t$. Hence

$$\epsilon\left[\frac{d\Sigma_E}{dt}\Delta t + \sigma'\Delta t\right] = \epsilon\Delta V + k\Delta t + \frac{d}{dt}(pv)\Delta t.$$

Now

$$\frac{d}{dt}(pv)\Delta t = k\Delta t.$$

Hence

$$\frac{d\Sigma_E}{dt} + \sigma' = \frac{dV}{dt} + \frac{\epsilon k}{t},$$

or

$$\frac{d\Sigma_E}{dt} + \sigma' = \frac{P_S}{t} - \frac{\epsilon k}{t},$$

the desired relation.

It is to be especially emphasized that the form of the formul obtained essentially modifies the point of view hitherto maintained. position up to this point in this paper has been one of agnosticis have been obliged to retain separate expressions for local E.M.F. and potential difference because there seemed no necessity that should be equal, although such equality is usually assumed. Bu the fact that the formulas obtained for

$$\frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{\epsilon P_S}{t}, \qquad \frac{d\Sigma_E}{dt} + \sigma' - \frac{P_S}{t}, \qquad \text{and} \qquad \frac{dV_E}{dt} + \sigma'$$

are of different form constitutes positive proof that local E.M.F. and potential difference cannot be mutually equal, and that the as tion of such equality is in general positively incorrect. The assu can be valid only in certain special cases, as in an electron gas.

Richardson has frequently set local E.M.F. and local heat eq each other. This is in general incorrect, but will not necessaril to error in those processes in which a complete cycle is described.

Accepting now as proved that in general local heat, potential ence, and E.M.F. cannot be mutually equal, we will, in the next s deduce additional relations between them.

The Generalized Volta Law of Tensions.

In a complete circuit composed of three metals in equilibri uniform temperature we have the following four relations:

$$V_{AB} + V_{BC} + V_{CA} = 0$$
$$S_{AB} + S_{BC} + S_{CA} = 0$$
$$\Sigma_{AB} + \Sigma_{BC} + \Sigma_{CA} = 0$$
$$P_{AB} + P_{BC} + P_{CA} = 0.$$

The first of these is a statement that the total change in electr potential in a closed path outside the metals is zero; the second same statement for a closed path within the metals; the third that the total E.M.F. in a circuit in the metal is zero; and the that the total heat absorbed in a cycle by electricity is zero. Th

two are a mathematical consequence of the properties of an electrostatic distribution, and the last two are a consequence of the law of the conservation of energy, because in a system of solids all at one temperature there is no permanent source of energy. It is not possible that these relations should not be satisfied; the system must of necessity so adjust itself that they are.

Of the four relations above, the first is the ordinary Volta law of tensions. The point of the Volta law is not that the laws of electrostatics or of the conservation of energy are satisfied, but that each of the quantities in the above equations, V_{BC} for example, depends only on the two metals B and C, and is unaffected by the presence in the circuit of the third metal A. The proof of this fact is given by experiment.

Of the four equations, the quantities in only two of them, the first and the last, are susceptible of direct observation. It is proved experimentally that P_{BC}, for example, as well as V_{BC}, is independent of the presence in the circuit of the third metal. Therefore the Peltier heats satisfy the same conditions as the Volta difference of potential.

By the "generalized" Volta law of tensions we shall understand the correctness of the four equations above, and in addition a statement that any of the four types of action at the surface of two meals is independent of the presence of a third.

The quantities entering the second and third equations above are not directly measurable, and it is therefore pertinent to inquire whether the generalized Volta law holds; that is, whether S_{BC}, for example, is independent of the presence of A. The answer to this question is yes. Although a direct experimental proof is at present impossible, a theoretical proof may be given, because of certain relations holding between S and Σ and V.

It may be proved mathematically that the ordinary Volta law as partly expressed in the first of the above equations demands that each of the quantities may be split up into two quantities, each depending on only one of the metals at the junction. That is, it is possible to write $V_{BC} = V_C - V_B$, where V_B depends only on the properties of B and V_C only on those of C. This analysis is physically significant because it represents the action at the surface of B and C as the joint result of independent actions by B and C, each unaffected by the presence of the other. The proof of the generalized Volta law will be given by similarly splitting each of the quantities above into the difference of two quantities, each depending only on the properties of one of the metals at the junction.

This analysis is immediately effected from the expression for V_{AB}.

We have

$$\frac{n_A}{n_B} = e^{\epsilon(V_{BA} - V)/kt},$$

Whence

$$V_{AB} = \frac{kt}{\epsilon} \log \frac{n_A}{n_B},$$

and we write at once

$$V_{AB} = V_B - V_A,$$

where

$$V_A = -\frac{kt}{\epsilon} \log n_A.$$

It is to be noticed that this analysis is not unique. We might equ write, for example,

$$V_A = -\frac{kt}{\epsilon} \log p_A,$$

which differs from the above by a quantity independent of A, depending on the temperature.

We may now split up the other quantities with the help of equat (18), (19) and (20).

$$P_{BA} = V_{BA} + \frac{\mathrm{I}}{\epsilon}(\eta p_B - \eta p_A) \quad P_A \quad P_B,$$

and

$$P_A = -\frac{kt}{\epsilon} \log n_A - \frac{\mathrm{I}}{\epsilon} \eta_{pA}$$

and

$$S_{BA} = V_{BA} - S_{AE} + S_{BE} \quad S_A \quad S_B,$$

$$S_A = -\frac{kt}{\epsilon} \log n_A - S_{AE}$$

and

$$\Sigma_{BA} = V_{BA} - \Sigma_{AE} + \Sigma_{BE} \quad \Sigma_A \quad \Sigma_B,$$

$$\Sigma_A = -\frac{kt}{\epsilon} \log n_A - \Sigma_{AE}.$$

With regard to the last two it is to be said that it is mathematica conceivable that S_{AE} and Σ_{AE} should depend on the presence of the oth metal, but physically it appears excessively improbable. Granting th assumption, this analysis shows that the generalized Volta law of tensio applies to the unmeasurable quantities S and Σ as well as to V and

Instead of the quantity Σ, we may, if we prefer, introduce the intrins energy of electricity, u, in the conductor. Taking the energy of a perfe gas to be zero at absolute zero of temperature, we obtain, on applyin

our definition of impressed E.M.F. between two points

$$\epsilon\Sigma_{AE} = \tfrac{3}{2}kt - \epsilon u_A + \epsilon S_{AE} + kt,$$

whence

$$\Sigma_{AE} = \tfrac{5}{2}kt - u_A + S_{AE}. \tag{40}$$

No simplification of the formulas is obtained on replacing Σ in terms of u. For theoretical discussions of the electron mechanism, however, it may be preferable to make this substitution.

THE EFFECT OF HYDROSTATIC PRESSURE ON THE VOLTA EFFECT.

The condenser analysis by which the effect of temperature on the Volta effect was determined may be modified to include the effects of hydrostatic pressure. The system of two metals A and B shall be characterized by the following variables.

t = absolute temperature,

ρ = positive charge per unit area on A (as before there is an equal opposite charge on B),

c = capacity per unit area,

π = hydrostatic pressure per unit area on the plate A (the symbol π is used for pressure to avoid confusion with p, the vapor pressure of the electron atmosphere).

There is no essential restriction in discussing the effect of a pressure applied to the plate A alone. After the formulas for this case have been developed, the effect of pressure on B alone may be found simply by interchanging the letters in the analysis, and then the effect of independently variable pressure on both A and B by adding the two effects.

The following dependent variables are to be discussed:

V_{BA} = Volta rise of potential on passing from B to A (see previous discussion for more detailed specification),

u = internal energy of system per unit area,

dW = work done by the system in any infinitesimal change,

dQ = heat absorbed by the system in any infinitesimal change,

v = volume of A per unit area.

Now, as before, we must have $(du + dW)/t$ an exact differential for reversible changes. We have

$$dW = \frac{\partial W}{\partial t}dt + \frac{\partial W}{\partial \rho}d\rho + \frac{\partial W}{\partial c}dc + \frac{\partial W}{\partial \pi}d\pi$$

and

$$du = \frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial \rho}d\rho + \frac{\partial u}{\partial c}dc + \frac{\partial u}{\partial \pi}d\pi.$$

We are able to completely calculate dW from our knowledge of the

mechanics of the system. We have

$$\frac{\partial W}{\partial t} = \pi \frac{\partial v}{\partial t},$$

$$\frac{\partial W}{\partial \rho} = -\left(\frac{\rho}{c} - V_{BA}\right) + \pi \frac{\partial v}{\partial \rho},$$

$$\frac{\partial W}{\partial c} = \frac{1}{2}\frac{\rho^2}{c^2} + \pi \frac{\partial v}{\partial c},$$

$$\frac{\partial W}{\partial \pi} = \pi \frac{\partial v}{\partial \pi}.$$

Substituting above,

$$\frac{1}{t}\left\{\left[\pi \frac{\partial v}{\partial t} + \frac{\partial u}{\partial t}\right]dt + \left[\pi \frac{\partial v}{\partial \rho} - \frac{\rho}{c} + V_{BA} + \frac{\partial u}{\partial \rho}\right]d\rho + \left[\frac{1}{2}\frac{\rho^2}{c^2} + \pi \frac{\partial v}{\partial \pi} + \frac{\partial u}{\partial c}\right]dc + \left[\pi \frac{\partial v}{\partial \pi} + \frac{\partial u}{\partial \pi}\right]d\pi\right\}$$

must be an exact differential. This will give us six relations between the coefficients of the six possible pairs of differentials.

The work for finding these derivatives is entirely straightforward; only the results need be given here.

From the coefficients of dt and $d\rho$,

$$\frac{\partial V_{BA}}{\partial t} = \frac{1}{t}\frac{\partial Q}{\partial \rho} = \frac{1}{t} P_{BA}'.$$

From the coefficients of dt and dc

$$\frac{\partial Q}{\partial c} = 0.$$

From the coefficients of dt and $d\pi$,

$$\frac{\partial Q}{\partial \pi} = -\tau \frac{\partial v}{\partial t}.$$

From the coefficients of $d\rho$ and dc,

$$\frac{1}{t}\frac{\partial V_{BA}}{\partial c} = 0.$$

From the coefficients of $d\rho$ and $d\pi$,

$$\frac{\partial V_{BA}}{\partial \pi} = -\frac{\partial v}{\partial \rho}.$$

From the coefficients of dc and $d\pi$,

$$\frac{1}{t}\frac{\partial v}{\partial c} = 0.$$

Of these six relations the three which do not involve $d\pi$, (41, 42 and 44) are the same as those obtained by the previous analysis, except that the partial derivatives now involve the condition of constancy of π, a variable which did not enter in the previous work. Of the three remaining relations, 46 states that there is no change of volume on merely changing the distance between the plates, and 43 gives the ordinary thermodynamic relation for the heat absorbed during a change of pressure, it now being necessary to add the conditions of constant ρ and c to the ordinary condition of constant t during change of pressure. The remaining relation, 45, is the only one of the six which gives any essentially new information. This equation expresses the change in Volta difference between two metals, when one is subjected to pressure, in terms of the change of volume of that metal when unit positive charge is imparted to it. This change of volume is not an electrostriction effect, which varies as ρ^2 and depends on the shape of the metals, but is to be thought of as the effective volume of the electrons added or subtracted. There seems to be no experimental evidence for even the order of magnitude of $\partial v/\partial \rho$.

Within the range in which $\partial v/\partial \rho$ may be regarded as constant, this formula gives the Volta contact difference of potential between compressed and uncompressed metal.

$$V_{0\pi} = -\pi \frac{\partial v}{\partial \rho}. \tag{47}$$

The formula

$$\frac{\partial V_{BA}}{\partial \pi} = -\frac{\partial v}{\partial \rho}$$

may also be obtained by considering the effect of hydrostatic pressure in A on the pressure of the electron vapor in equilibrium with it through a stress resisting membrane. The formulas to be applied are well known; they may, for example, be obtained as special cases of formulas which I have given in a previous paper (21). The applicability of such formulas to such conditions as these becomes at least questionable, however, when one calculates that the density of the electron vapor in equilibrium with tungsten at 0° C., for example, is such that there is one electron in a sphere of radius 350 light years. The method of analysis used above makes no reference to the electron gas, and leads to the same results for those quantities not directly concerned with the vapor.

Effect of Pressure on Thermo-electric Properties.

A certain amount of information may now be obtained regarding the effect of pressure on thermo-electric properties other than the Volta

effect. This may be obtained from the formulas previously given, taking as the metals A and B the same metal in two states, one without pressure and the other with it. The same double subscript notation as before may be used. Thus $S_{0\pi}$ denotes the potential jump in passing within the metal through the surface separating uncompressed metal from metal compressed to the pressure π.

For the Peltier heat in passing from uncompressed to compressed metal in terms of the E.M.F. of a couple composed of uncompressed and compressed metal, formula 3 gives

$$P_{0\pi} = t \frac{dE_{0\pi}}{dt}. \tag{48}$$

For the difference between the Thomson heats in the compressed and uncompressed metal, formula 4 gives,

$$\sigma_\pi - \sigma_0 = t \frac{d^2E_{0\pi}}{dt^2}. \tag{49}$$

For the effect of pressure on the density of an electron gas in equilibrium with a compressed metal formula 12, combined with formula 47 for the Volta difference of potential between compressed and uncompressed metal, gives

$$\frac{1}{n}\frac{\partial n}{\partial \pi} = \frac{\epsilon}{kt}\frac{\partial v}{\partial \rho}. \tag{50}$$

For the effect of pressure on the latent heat of vaporization of electrons under variable surface charge (total charge on metal and in the gas remaining constant) formula 13 gives

$$\eta_\pi - \eta_0 = \epsilon V_{0\pi} - \epsilon t \frac{dV_{0\pi}}{dt}. \tag{51}$$

For the effect of pressure on the latent heat of vaporization at constant surface charge formula 14 gives

$$\eta_{\rho\pi} - \eta_{\rho 0} = \epsilon(V_{0\pi} - P_{0\pi}). \tag{52}$$

For the effect of pressure on the surface heat, we get from 11 and 51 and 52

$$P_S(\pi) - P_S(0) = t \frac{dV_{0\pi}}{dt} - P_{0\pi}. \tag{53}$$

Of the six quantities treated in the last six equations, the first two, namely the effect of pressure on Peltier and Thomson heats, have been determined experimentally (1) from measurements on a "pressure" thermo-couple. The last four, namely the effect of pressure on electron gas density, the two latent heats, and the surface heat, cannot at present

be determined numerically, because they involve the "pressure" Volta effect ($V_{0\pi}$) in addition to the "pressure" Peltier heat ($P_{0\pi}$). A determination of the pressure Volta effect, in addition to present knowledge, would give immediately all four of these quantities. Of course there are relations between the effects of pressure on these four quantities which may be obtained by eliminating $V_{0\pi}$ and $P_{0\pi}$ between the several equations.

In addition to the pressure effects 48–53, we may also obtain expressions for the effect of pressure on the various potential jumps and surface E.M.F.'s, but these can no longer be determined in terms only of $E_{0\pi}$ and $V_{0\pi}$, but involve an actual determination of some potential jump or surface E.M.F., which we are not yet in a position to make.

For the potential jumps, formula 19, gives

$$(S_{\pi E} - S_{0E}) + S_{0\pi} = V_{0\pi}. \tag{54}$$

For the surface E.M.F.'s, formula 20 gives

$$(\Sigma_{\pi E} - \Sigma_{0E}) + \Sigma_{0\pi} = V_{0\pi}. \tag{55}$$

For the Thomson potential gradient, formula 23 gives

$$\sigma_\pi'' - \sigma_0'' = \frac{dS_{0\pi}}{dt} - \frac{dE_{0\pi}}{dt}. \tag{56}$$

For the Thomson E.M.F., formula 21 gives

$$\sigma_\pi' - \sigma_0' = \frac{d\Sigma_{0\pi}}{dt} - \frac{dE_{0\pi}}{dt}. \tag{57}$$

Formulas 28, 30 and 31 give nothing new when applied to pressure effects.

With regard to the quantity $V_{0\pi}$ $(= -\pi \cdot \partial v/\partial \rho)$, we can possibly obtain an idea of the order of magnitude within 100 or 1,000 fold by assuming that all the change of volume on imparting a charge to a metal is the volume of the electrons added. Assuming that the radius of an electron is 1.8×10^{-13}, this gives for a lower limit

$$\frac{\partial v}{\partial \rho} = -1.7 \times 10^{-19} \text{ c.c.}$$

per coulomb. This is so excessively minute that the actual $\partial v/\partial \rho$ is probably forever beyond the reach of direct observation.

In view of the extreme smallness of the probable effect of pressure on the Volta potential difference it is natural to inquire whether we may not neglect this effect in comparison with the directly measurable $P_{0\pi}$, and so obtain an approximate idea of the order of the effect of pressure on the quantities given in equations 50–53. It turns out that this is

probably not allowable. The experimental data give for molybdenum, for example, the value 1.5×10^{-18} for the effect of 1 dyne pressure on the Peltier heat. For most metals, the effect is of the order of 10 times greater, or 100 times the volume effect as calculated above from the volume of one coulomb of electrons. In view, however, of the extreme uncertainty in this latter value, I do not believe that a margin of 100 fold is sufficient, and that we would be justified in neglecting the effect of pressure on Volta effect in comparison with that on Peltier heat.

Effect of Melting or Change of State on the Volta Potential Difference and Thermo-electric Phenomena.

The Volta difference of potential between a metal in two states of aggregation, as for example solid and liquid, may be found by a slight modification of the preceding condenser analysis. This may be done by choosing for the independent variables t, ρ, c and volume, instead of t, ρ, c and pressure. The details of the work are the same as before. Six differential relations are obtained as before. The only essentially new one of these is

$$\left(\frac{\partial V_{BA}}{\partial v}\right)_{t,\rho,c} = \left(\frac{\partial \pi}{\partial \rho}\right)_{t,c,v}. \tag{58}$$

If this equation is applied to melting or other change of state, we have the statement that the change in Volta contact difference of potential between B and A when A melts is equal to the change of volume on melting multiplied by the change in the melting pressure of A when unit quantity of electricity is added to the exterior surface of A at constant temperature, volume, and capacity. In virtue of the Volta law of tensions, this becomes, if we denote the two phases by subscripts 1 and 2,

$$V_{21} = (v_1 - v_2)\left(\frac{\partial \pi}{\partial \rho}\right)_{\tau}. \tag{59}$$

The effect of a surface charge on melting point is one on which there seems to be no experimental evidence. It is not probable that a charge on the surface could change the equilibrium conditions between liquid and solid at points within the metallic mass, for there is no electric field at such points, and there is no real charge on a surface of separation of solid and liquid metal. It is possible, however, that a surface charge should have a surface effect on melting. For instance, the charged surface of a solid metal might possibly melt at a lower temperature than the interior, or conversely, the charged surface of a liquid might solidify at a higher temperature than the interior.

We may obtain partial information as to the effect of a change of state on the other thermo-electric and thermionic quantities by using the subscripts A and B of the first sections of this paper for the same metal in two different states of aggregation. The work is exactly similar to that of the section on pressure effects, and a series of formulas would be obtained parallel to 48–57.

Very little experimental work has been done in this field. So far as I know there are no measurements of the Volta potential difference between solid and liquid metal, so that there is no way at present of telling the order of magnitude of certain of the quantities in the above equations. Experiments have been made, however, on the thermal E.M.F. of closed circuits in which one of the metals passes through the melting point. There has been considerable disagreement about the facts, but the latest work (22) seems definitely to establish that there is a discontinuous change in the direction of the E.M.F. curve on melting. Attempts have been made to deduce from these data information as to the behavior of the Volta effect, etc., but all such attempts have involved some of the special assumptions about equality of local E.M.F.'s, heats, and potential differences which we are unwilling to admit.

Hitherto the electron theory has been unsuccessful in explaining the effects on melting, in most every case giving the wrong sign to the effect.

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An Experiment in One-piece Gun Construction

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(New York Meeting, February, 1920)

During the war, the Navy undertook the construction, under my direction, of an experimental gun embodying features designed to lessen the cost and time of production. These experiments were initiated after representations as to their desirability had been offered by myself, by the Naval Consulting Board, and by the National Research Council. The first drawings were made in June, 1917, and the experiment was completed in November, 1918.

For the sake of clearness it will pay to recapitulate briefly the fundamental idea of gun construction. It is well known that if a hollow cylinder is subjected to internal fluid pressure, the maximum stress occurs in the inside layers, the outer parts carrying much less than their due share of the stress. This inequality of stress is more pronounced the thicker the walls of the cylinder. If such a cylinder is pushed to the elastic limit, failure in elasticity will take place long before the outer layers have reached the limit of their capacity. Economical use of the material would demand, however, that all parts of the cylinder reach the limits of their capacity simultaneously. This may be brought about, at least in cylinders of not too great thickness, by producing in the inner layers an initial compression, and in the outer layers an initial tension. The effect of internal pressure is at first to relieve the compression of the inside layers, while increasing the tension of the outside layers. If the initial stresses are properly distributed, all parts of the cylinder will reach their elastic limits simultaneously, thus giving a cylinder of maximum strength for its weight.

In gun construction as hitherto practiced, this initial distribution of stress is produced either by winding the inner tube with wire, a common English practice, or by shrinking hoops over the inner tube, which has been the standard American practice. Either process is long and expensive, particularly with the larger guns, 12- or 14-in., which require

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seven or eight hoops at the breech, each of which must be machined inside and outside to one or two thousandths of an inch.

There is another possible method of producing the desired internal compression. If a heavy cylinder is stretched considerably beyond its elastic limit, the inner layers flow and the outer layers receive a permanent stretch. On release of pressure, the outer layers shrink back on the inner, producing an internal compression, and, of course, an equilibrating tension in the outside layers. If now pressure is reapplied, it will be found that the elastic limit has been raised to the previous maximum pressure. It is possible to raise the limit in this way to two or three times the value as calculated by the usual theories. This behavior of cylinders under high internal pressure was demonstrated experimentally, and has been continually used in the construction of apparatus for my high pressure experiments at the Jefferson Physical Laboratory, since 1906. In these experiments I have accurately measured hydrostatic pressures as high as 300,000 lb. per sq. in. (21,090 kg. per sq. cm.), pressures which would have been unattainable except for this behavior of thick cylinders when stretched beyond the elastic limit.

The entire subject of the stress-strain relations in metal strained beyond the elastic limit is at present beyond the reach of theory; for instance, if a heavy cylinder is pushed to eventual rupture the crack starts at the outside instead of the inside surface, so that it is not possible to compute exactly the distribution of stress in a cylinder stretched as above, but approximate theory indicates a distribution of stress much like that of a built-up gun, and it is obvious at any rate that at the maximum pressure all parts of the gun must be pretty near the limit of their capacity. The application of this laboratory method to gun construction was obvious, and I had long had it in mind.[1] The procedure is to start with a single forging of approximately the dimensions of the finished gun, subject it to internal pressure (in one or more stages, depending on the external shape) high enough to stretch it permanently, and thus raise the elastic limit by producing a compression in the inside layers and a tension in the outside layers, and then to machine it to final dimensions. The pressures expected for the steels of ordinary gun construction would be of the order of 100,000 lb. per sq. in. (7030 kg. per sq. cm.). The firing pressure of a large gun is of the order of 30,000 lb. per sq. in. (2109 kg. per sq. cm.).

On examination, it appeared that the fundamental idea of raising the elastic limit by permanently stretching with an internal application of high pressure was very old. The Austrians tried, in the eighteenth century, to accomplish it by forcing a steel expanding mandrel through the bore of the gun; there are English and French patents dating back to

[1] *Phil. Mag.* (July, 1912) **24**, 78.

the 1870's, and in this country there are the Emery patents between 1900 and 1904. There is also a theoretical paper by Turner.[2] None but the Austrians, however, had attempted to apply the idea in practise, and this fact was doubtless partly responsible for much of the scepticism as to the correctness of the fundamental idea that was felt in various quarters. The probable reason why the idea had not been practically applied was the technical difficulty of making packings leak-proof at the pressures required. In my experiments, however, I had developed a technique by which pressure could be controlled up to the limit of the strength of the containing vessel.[3]

Just before the completion of the experiments, a report came that the French had succeeded, during the war, in reducing to successful practice the same idea by a method somewhat similar, and had in use, on the firing line, guns so constructed. The details of the method were not imparted, but it is probable that the stretching was performed by firing abnormally heavy powder charges in the gun.

From a purely scientific point of view, the proposed demonstration of the possibility of the process was superfluous, in view of the laboratory experiments, but from an engineering point of view it was possible that there might be unforeseen difficulties in getting homogeneous forgings of a large enough size, or that other obstructions might arise in passing from small- to large-scale work. In any event, an engineer finds it hard to resist a certain satisfaction in a large-scale demonstration which he does not entertain for an experiment of more academic dimensions.

The experiments were entirely successful, and the correctness of the fundamental ideas and the feasibility of construction were proved. The gun actually experimented with was a 3-in. (76 mm.), 23 caliber gun. A larger gun, either in bore or in length, would have been desirable, but the forging for this gun was the largest that the Washington Navy Yard could make, and the Navy Department was unwilling to interfere with production by asking any outside concern for a larger forging. After treatment and final machining, the gun was successfully tested for nine rounds at 21.8 tons per sq. in. (3065 kg. per sq. cm.). The usual test for a gun of this size is three rounds at a slightly less pressure. The pressure, in actual firing, is only 13 tons per sq. in. (1828 kg. per sq. cm.). With regard to cost and ease of manufacture, the following extract is taken from a report of the Commandant and Superintendent of the Naval Gun Factory, to the Bureau of Ordnance. "From this summary, it would seem that the actual saving of money would be inconsiderable for this type of gun, but it is undoubtedly certain that the saving of time, if quantity production should be attempted on this basis, would be enor-

[2] *Trans.* Cambridge Phil. Soc. (Sept., 1910).

[3] See Technique of High Pressure Experimenting. *Proc.* Amer. Acad. (Feb., 1914)

mous. Further, in the larger-type guns, it is thought that the simpler operations would involve the saving of a considerable amount of money as well as time."

Apart from proving the feasibility of gun construction by this method, the experiment has engineering interest concerning the means taken for controlling pressure of the required magnitude, and with regard to the elastic behavior of thick cylinders under high internal pressure.

The general scheme of the apparatus was as follows: the gun was plugged at both ends, one of the plugs being perforated to make connec-

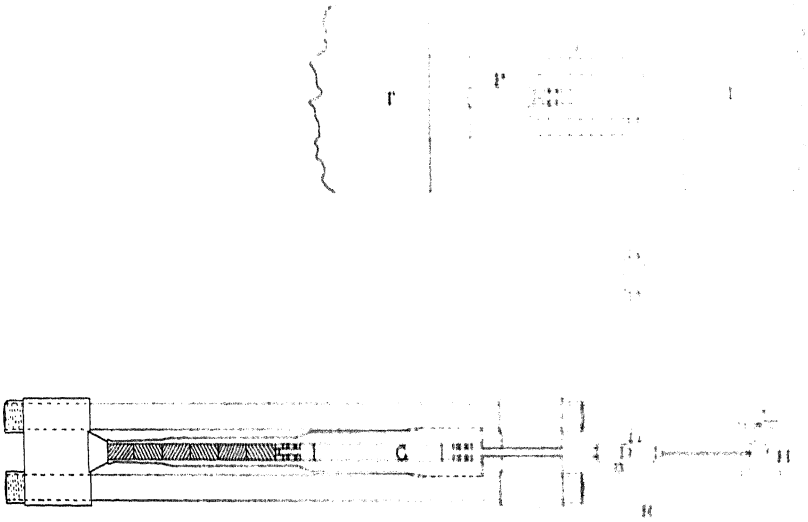


FIG. 1.—GENERAL ASSEMBLY VIEW. PRESSURE IS PRODUCED IN CYLINDER C BY PUSHING PISTON *P* WITH HEADS OF TESTING MACHINE *T*. PRESSURE IS TRANSMITTED THROUGH CONNECTING PIPES TO INTERIOR OF GUN *G*. WIRES *R* ARE CONNECTED TO MANGANIN RESISTANCE CAGE. INITIAL PRESSURE IS PRODUCED BY HAND PUMP *H*.

tion with a pipe leading to a cylinder and piston placed between the jaws of a hydraulic press. The interiors of gun and cylinder were filled with a suitable fluid, and any desired pressure was produced by operating the press.

No attempt was made to set up an apparatus capable of immediate commercial use; in this first experiment, the sole object was to show the correctness of the fundamental idea, and to that end the experimental set-up was designed so as to be simple and inexpensive using, so far as feasible, resources already available. A general assembly view of the apparatus is shown in Fig. 1. For the press with which the piston was driven into the cylinder, the 2,000,000-lb. (907,200-kg.) Emery testing machine of the Bureau of Standards was used, the machine being set up for tests in compression. The use of the Emery machine made it necessary to perform the actual stretching of the gun at the Bureau of Standards. I have to thank Dr. Stratton, Director of the Bureau, for the use

of the press and the most courteous way in which the resources of the Bureau were placed at my disposal.

In Fig. 1 the testing machine is indicated by the two press heads; in use, the right-hand head was stationary, the left-hand head moving toward it, driving the piston into the cylinder. The interior diameter of the cylinder was 3 in. (76.2 mm.). The area of a circle of this diameter is 7.07 sq. in. (45.6 sq. cm.) so that the estimated pressure of 100,000 lb. per sq. in. (7030 kg. per sq. cm.) in the gun would require a thrust of 707,000 lb. (320,685 kg.), exclusive of friction, on the piston. The necessity of a large press is therefore evident. The cylinder was made in two parts. The central part was 22 in. long and 8 in. in diameter (56 by 20 cm.), of Cr-Ni steel having an ultimate strength of 275,000 lb. per sq. in. (19,332 kg. per sq. cm.) and elastic limit of 240,000 lb. (16,872 kg. per sq. cm.) with an elongation of 5 per cent. Over this central core were shrunk eight rings of the same steel, 15 in. (38 cm.) outside diameter, and 2 in. (5 cm.) thick. It was necessary to build up the cylinder in this way in order that all the metal parts might be comparatively thin, so that the effect of heat treatment might extend throughout the mass of the metal. The piston was of glass-hard tool steel, 13 in. long and 2.995 in. diameter (33 by 7.607 cm.). I have found in all my work that pistons which are to take a pure thrust are much better left glass-hard.

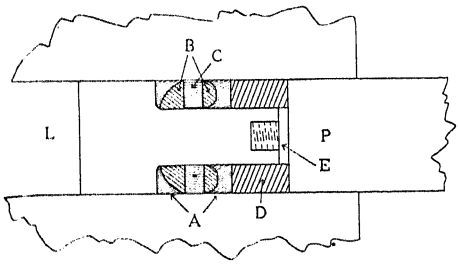


FIG. 2.—DETAILS OF PACKING PLUG OF CYLINDER. PISTON *P* PUSHES PLUG TOWARD LIQUID AT *L*. *A* IS SOFT STEEL, *B* SOLDER, *C* SOFT RUBBER, *D* HARDENED STEEL. *E* IS UNSUPPORTED AREA BACK OF THE PLUG.

The packing plug, driven by the piston into the cylinder, is shown in Fig. 2. Its principle is such that the pressure in the packing is automatically maintained any desired percentage higher than the pressure in the liquid, making leakage impossible. It has been fully described in the paper on technique already cited. The plug consists essentially of a plunger with a stem, the packing, which is ordinary soft rubber, being placed around the stem. The rear end of the stem slides in a hardened steel ring of such thickness that this end of the stem is left without longitudinal support. The principle of operation is as follows. Since the plunger is in equilibrium at any stated pressure, the total force exerted by the liquid in one direction on the plunger head must be balanced by the total force in the other direction exerted by the annular shaped pack-

ing. But the area on which the liquid acts is greater than that on which the packing acts, so that the intensity of pressure in the packing is greater than that in the liquid. In particular, if the diameter of the stem is one-half that of the plunger head, the area of the ring is 75 per cent. that of the head, so that the pressure in the packing is 33 per cent. greater than that in the liquid. This principle of an unsupported area (in this case the free end of the stem shown at *E*) is capable of the most varied modification, and by the use of it any problem in high-pressure packing may be solved. In Fig. 2 the various auxiliary packing rings of steel or solder keep the rubber in place.

The connecting pipe leading from the cylinder was 1¼ in. (3.18 cm.) outside diameter, and ⅛ in. (3.2 mm.) inside diameter. It was made of the same Cr-Ni steel as the cylinder, drilled from the solid rod, and turned to final dimensions, on centers, after drilling. Because of the difficulty of drilling longer holes of a diameter smaller than ⅛ in., the pipe was made in 30-in. lengths. Two lengths were necessary to lead from the cylinder to the axis of the gun, and these were connected by a right- and left-handed coupling, of obvious design. The packing at the ends of the pipe used the same principle of unsupported areas as just described, but the details were different, the packing material in this case being soft-steel rings. The details of this pipe packing have been shown in Fig. 10, page 639, of the paper on technique.[4]

The gun is shown in position in a heavy steel yoke, by which the plugs at both ends were prevented from blowing out. The two ends of this yoke were forgings of mild steel, 21 in. (53 cm.) square and 12 in. (30 cm.) thick. There were four tie rods of mild steel, 5 in. (12.7 cm.) in diameter and 9½ ft. (2.9 m.) long. The right-hand head of the yoke was pierced centrally to allow entrance of the connecting pipe to the breech of the gun. This pipe made connection at one end to a right-angled coupling piece *D*, to which the pipe was brought from the cylinder, and at the other end connected with the interior of the gun. The packing on the gun end of this pipe was essentially like that shown for the cylinder. The stem of the plunger was here replaced by the straight shank of the connecting pipe, and the head of the plunger by a head turned on the pipe. The packing plug at the muzzle end of the gun was essentially a duplicate of that for the cylinder, except that the conical steel parts were made longer and more tapering to take up the stretch during application of pressure. Some means of providing for a follow-up by the packing during stretch is essential, and the method shown was entirely successful.

The right-angled coupling *D*, besides connecting the pipes from cylinder and gun, contained two other essential parts of the apparatus. At the right-hand end of this coupling, connection was made through a check valve to a hand pump, the function of which was to produce an

[4] *Proc.* Amer. Acad., Feb., 1914.

initial pressure throughout the apparatus before the press started to drive the piston into the cylinder. Without this precaution, so much of the stroke of the piston would have been wasted in squeezing out air bubbles and in giving the initial rather large compression to the transmitting liquid, that it would not have been possible to reach the desired maximum pressure in the one stroke to which the apparatus was limited. The hand pump, which was one I had specially constructed for my experimental work, gave an initial pressure of 20,000 lb. per sq. in. (1406 kg. per sq. cm.).

The check valve was of obvious design, consisting of a carefully ground, hardened steel cone of about 90° angle, held tightly against its seat by a very heavy spring. It probably was not absolutely leak tight, but any leakage was not fast enough to be perceptible with apparatus of this scale, although it might be more troublesome with smaller apparatus.

Beside the connection to the low-pressure pump, the right-angled coupling contained the device for measuring pressure. It would have been easier if the pressure could have been computed from the area of the piston and the total thrust on the jaws of the testing machine, but the friction was so great as to make this impossible. For instance, at an actual pressure in the gun of 80,000 lb. per sq. in., the calculated pressure, making no allowance for friction, was 110,000 lb., showing a loss by friction of 30,000 lb. per sq. in. (27.3 per cent. of the calculated) or 210,000 lb. total thrust in the machine. It was therefore, necessary to measure the pressure in the gun directly. For this measurement, no ordinary type of gage, such as a Bourdon, is suitable, because of insufficient strength and too great elastic hysteresis. In my laboratory experiments, I had successfully used a manganin resistance gage, and this was used successfully here. This method of measuring pressures utilizes the change in resistance of a metal under pressure. Manganin is particularly suitable because of the linearity of the relationship, and the negligible effects of temperature changes. The magnitude of the variation in resistance is about 1.6 per cent. for 100,000 lb. per sq. in. (7030 kg. per sq. cm.). With modern commercial apparatus, a change of this magnitude may be easily measured with the required accuracy. Details of the method may be found on page 640 of the paper on technique,[5] and also in another paper.[6] For the actual details of the method of measuring resistance employed in connection with this gage, and for the apparatus, I am indebted to E. L. Purrington, of the Bureau of Standards.

The approximate dimensions of the gun, of a type now superseded, are shown in Fig. 3. This gun is especially simple in that the outside,

[5] *Loc. cit.*

[6] The Measurement of Hydrostatic Pressures up to 20,000 kg. per Square Centimeter. *Proc.* Amer. Acad. (Dec., 1911) **47**.

over the region in which the greatest powder pressure is exerted, consists of two cylinders of outside diameters 7.5 and 5.3 in. (19 and 13.5 cm.), respectively. The extreme muzzle, which is conical, need not be considered, because when the projectile has reached this part of the gun, the powder pressure has dropped so low as to make unnecessary any treatment of this portion.

It was necessary to apply the pressure in two stages, first to the breech alone, and second to the muzzle and breech, because a pressure high enough to stretch the breech sufficiently would have stretched too much and probably ruptured the muzzle. The two-stage application of pressure was accomplished as follows. The packing toward the muzzle was first placed at the region of decrease of outside diameter from 7.5 to 5.3 in., and held in this position by hardened steel blocks filling up the rest of the bore of the gun to the extreme muzzle. Thrust was transmitted through these blocks to the left-hand head of the yoke. The region open to pressure was thus restricted to the breech end of the gun, which thereupon stretched

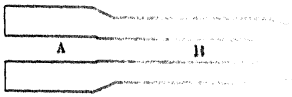


FIG. 3.—SCALE DRAWING OF THE GUN BEFORE TREATMENT. THE OVERALL LENGTH IS 77 IN. (195.6 CM.) INSIDE DIAMETER AT *A*, 2.7 IN. (6.86 CM.); INSIDE DIAMETER AT *B* 2.6 IN. (6.6 CM.), AND OUTSIDE DIAMETER 7.5 IN. (19 CM.); INSIDE DIAMETER AT *C* 2.6 IN. AND OUTSIDE DIAMETER 5.3 IN. (13.5 CM.).

to the required amount. Pressure was then released, the blocks retaining the left-hand packing plug were removed, and pressure was reapplied. The left-hand packing, now unsupported, was driven to the left by the pressure until stopped by the left-hand head of the yoke, leaving the breech and the muzzle accessible to pressure, which was then reapplied with sufficient force to stretch the muzzle. This pressure being less than that previously applied to the breech, because of the smaller dimensions of the muzzle, no additional permanent effect was produced at the breech.

The packing evidently had to be of such design that it would allow considerable stretch of the inside without leak, and could be moved from one position to the other without too great force and without leakage; it must also be used a second time in the new position, again without leak. The packing here illustrated satisfactorily answered these requirements. The maximum pressure required to overcome its friction was 35,000 lb. per sq. in. (2460 kg. per sq. cm.) and after the sticking point was passed a pressure of 2000 lb. per sq. in. moved it easily.

The details of the actual stretching were as follows. Four applications of pressure in all were made. The first of these, to the breech alone, was made on June 20, 1918, with unsuccessful results. Through

some misunderstanding, the kerosene specified as the filling fluid was not provided, and it was necessary to use a substitute having untried properties. The danger was that the oil might freeze under the high pressure, and thus refuse to transmit the pressure. This was actually what happened. The total thrust applied by the Emery machine was 1,300,000 lb., corresponding to 180,000 lb. per sq. in. in the cylinder, making no allowance for friction; of this pressure, only 95,000 lb. per sq. in. was recorded by the manganin gage, and, judging by the elastic behavior, only 78,000 lb. reached the inside of the gun. Under the extreme thrust, the pipe ruptured at the end nearest the cylinder, the cylinder itself was somewhat scored on the inside, and the piston was slightly upset. Repairs were made, and the next application of pressure, this time with the proper transmitting medium, was made to the breech on July 26, 1918. On the morning of July 27 the packing was driven back to the muzzle, and in the afternoon pressure was applied to both breech and muzzle, stretching the latter. On the morning of July 29, pressure was reapplied to the entire gun as a check on the raising of the elastic limit. The gun was then dismantled and sent to the Naval gun factory for finishing. It was turned, inside and out, rifled, the breech mechanism put in place, and the final firing tests, already mentioned, were made late in November, 1918.

The manner of yield during application of pressure now remains to be described as this offers some interesting features relating to the strength of materials. Measurements to 0.0001-in. (0.0025 mm.) were made with a micrometer on the outside diameter of the gun at a number of points, during and after each application of pressure, and on the inside diameter before and after the complete treatment. Interest in the results themselves would have warranted more careful measurements, but I did not feel justified in making a more elaborate study than was demanded by the needs of the moment.

In Fig. 4 is shown the relation between external diameter (mean of three readings at the center of the breech section) and pressure, during the initial application of pressure to the breech on June 20. Beyond 55,000 lb. per sq. in. the observed curve showed a break, due to the incipient freezing of the transmitting oil, so that the recorded pressures corresponding to the measured diameters were too high. It is possible, however, to estimate, from the behavior on the next application of pressure, that a maximum pressure of 78,000 lb. per sq. in. (5483 kg. per sq. cm.) was reached on the first application. The probable course of the true curve between 55,000 and 78,000 is shown dotted in the figure. A total set of 0.0037 in. (0.094 mm.) on the outside diameter was produced by the first application. The feature of particular interest in Fig. 4 is that there is no evidence of an elastic limit anywhere, on increasing pressure, but the stress-strain curve from the beginning shows pronounced curvature.

This is not surprising in this material, which could not have been left by the forging in a state of complete ease.

The linear relation to be expected between stress and strain in a cylinder of these dimensions may be computed from the theory of elasticity

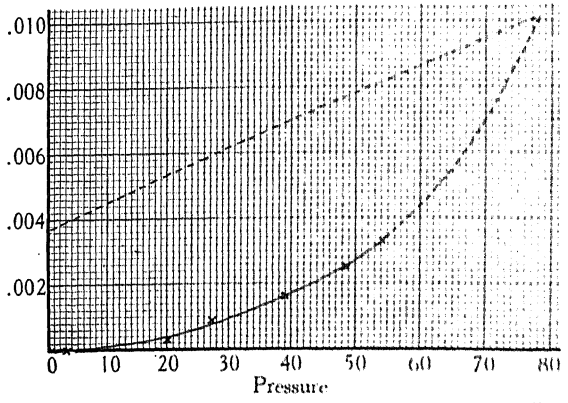


FIG. 4.—FIRST APPLICATION OF PRESSURE TO THE BREECH. THE INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST THE INTERNAL PRESSURE (ABSCISSA) IN THOUSANDS OF POUNDS PER SQUARE INCH.

as given in any textbook. (See, for example, Love's "Elasticity," p. 141.) We have for the radial displacement U,

$$U = Ar + \frac{B}{r}, \qquad A = \frac{pr_1^2}{2(\lambda + \mu)(r_0^2 - r_1^2)} - \frac{\lambda e}{2(\lambda + \mu)}.$$

$$B = \frac{pr_0^2 r_1^2}{2\mu(r_0^2 - r_1^2)}.$$

where p is the internal pressure, r_1 internal and r_0 external radius, λ and μ the two elastic constants. The longitudinal strain of the cylinder e is connected with the longitudinal fiber stress Z_z by the relation

$$Z_z = \frac{\lambda}{\lambda + \mu} \frac{pr_1^2}{r_0^2 - r_1^2} + e \frac{(3\lambda + 2\mu)\mu}{\lambda + \mu}.$$

In a cylinder mounted, as this was, so that the thrust on the end plugs was taken by an outside frame, we have, neglecting friction, $Z_z = 0$.

Taking as average values for the elastic constants of steel

$$\left.\begin{aligned} \mu &= 8.2 \times 10^{11} \\ \lambda &= 1.12 \times 10^{12} \end{aligned}\right\} \text{Abs. C. G. S. units,}$$

we find that $e = -2.59 \times 10^{-4}$ for 100,000 lb. per sq. in. That is, the gun shortens under internal pressure applied as above. With this value for e, we find

$$\left.\begin{aligned} A &= 3.18 \times 10^{-4} \\ B &= 3.31 \times 10^{-3} \end{aligned}\right\} \text{ for 100,000 lb. per sq. in.}$$

Substituting now the numerical values of 7.5 in. for the outside diameter, and 2.6 in. for the inside diameter (the gun was made 0.4 in. small on

the inside to allow for stretch) we find $U = 3.4 \times 10^{-3}$ for 100,000 lb per sq. in. That is, the outside diameter should increase 0.0068 in (0.173 mm.) under 100,000 lb. per sq. in. (7030 kg. per sq. cm.) interna pressure. The slope of the initial part of the curve in Fig. 4 is much les than this, while that of the latter part during stretch is, of course, muc greater. The recovery after release of pressure was, however, at th rate of 0.0080 in. (0.203 mm.) per 100,000 lb. That is, the first applica

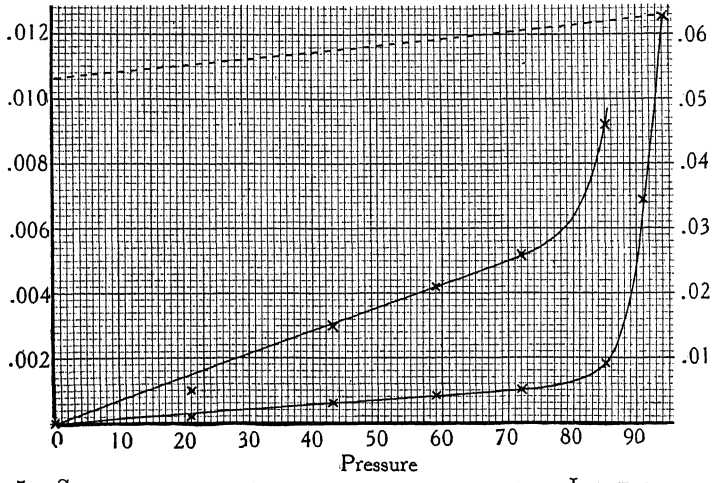


FIG. 5.—SECOND APPLICATION OF PRESSURE TO BREECH. INCREASE OF OUTSI DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST INSIDE PRESSURE (ABSCISSA) THOUSANDS OF POUNDS PER SQUARE INCH. RESULTS ARE SHOWN ON TWO SCALE LEFT-HAND SCALE APPLIES TO UPPER CURVE, WHICH SHOWS STRAIN BEFORE PR NOUNCED FLOW HAS BEGUN, AND RIGHT-HAND SCALE APPLIES TO LOWER CURVE, WHI SHOWS STRAIN DURING BOTH STAGES OF ELASTIC YIELD AND OF FLOW.

tion of pressure, in spite of some permanent set, has left the metal wit effective elastic constants approaching those of a state of ease.

The elastic limit to be expected on the maximum stress theory ca be easily computed. At the inner surface we have

$$\Theta_\theta = \frac{r_0^2 + r_1^2}{r_0^2 - r_1^2} p,$$

where Θ_θ is the circumferential fiber stress. The elastic limit of this ste was about 60,000 lb. per sq. in. (4218 kg. per sq. cm.). Substituting th value for Θ_θ gives 46,500 lb. per sq. in. (3269 kg. per sq. cm.) as the e pected elastic limit of a cylinder initially without internal stress and in state of complete ease.

The results of the second application of pressure to the breech, July 26, are shown in Fig. 5. Pressure was pushed to a maximum 94,000 lb. per sq. in. (6609 kg. per sq. cm.) producing an additional perm nent set of 0.053 in. (1.35 mm.) on the outside. This additional set too

place almost entirely above 85,000 lb. In the diagram, the results are plotted on two scales; on a large scale showing the results to 85,000 lb., and on a scale five times smaller to show the flow and set. It is evident that the initial stress-strain relation is much more nearly linear on the second than on the first application of pressure. The best straight line through the points up to 73,000 lb. has a slope of 0.0072 in. per 100,000 lb., which is close to the theoretical elastic rate. The rate of recovery after release of pressure was at the rate of 0.0103 in. per 100,000 lb., which is considerably more than the elastic rate. This is to be explained by hysteresis effects, which are always especially prominent in metal which has been recently severely strained.

The stress-strain relations on the next application to the breech, on July 27, are shown in Fig. 6. The muzzle was being treated during this application, so that it was not possible to reach the old maximum of

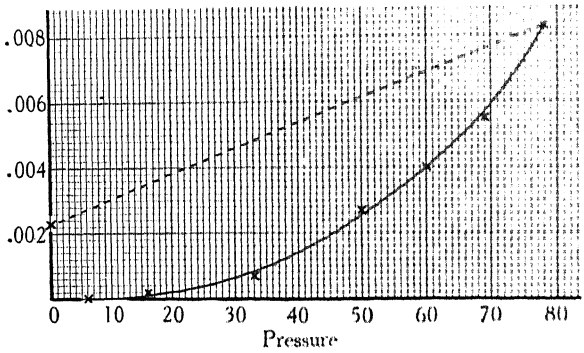


FIG. 6.—THIRD APPLICATION OF PRESSURE TO THE BREECH. THE INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST THE INTERNAL PRESSURE IN THOUSANDS OF POUNDS PER SQUARE INCH.

94,000 lb., 78,000 lb. (5483 kg. per sq. cm.) being all that was required to give the muzzle the desired stretch. The breech received an additional stretch of 0.0023 in. (0.058 mm.) during this third application. The stress-strain relation shows just as pronounced curvature as it did on the first application. This is evidently an effect of the previous severe straining and considerable flow produced by 94,000 lb.; the interior of the metal had been thrown into a state of disturbed internal equilibrium. A state of ease may be recovered after such treatment by prolonged resting; it is also known that the speed of recovery is greatly increased by moderate heating. The elastic recovery on release of pressure after the third application was at the rate of 0.0076 in. per 100,000 lb., again approaching the theoretical rate.

The results of the fourth application to the breech, on July 29, are shown in Fig. 7. One observed point was discarded because it was so far off the curve that it was evident that a blunder had been made in reading.

Two readings were made with decreasing pressure, an observation not previously made. The relation between stress and strain is now much more nearly linear. The whole cycle of operations forms an open hysteresis loop, such as are quite characteristic of the behavior of heavy masses of metal strained far beyond the elastic limit. I have elsewhere[7] shown examples of such loops obtained under other conditions. The permanent stretch, after this fourth application, was only 0.0007 in. (0.018 mm.). In such cases as the present, the conventional terminology breaks down, but it is to be questioned whether such slight permanent alterations of dimensions as have been shown after the first, third, and fourth applications of pressure are correctly characterized as set, proper, in the understood sense of the word, but are not rather to be recognized as a result of the internal accommodation that has evidently taken place, as shown by the character of the stress-strain curve under increasing stress.

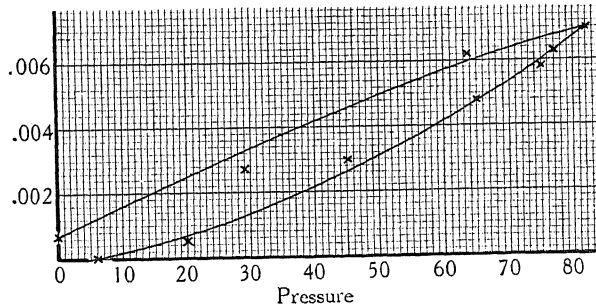


FIG. 7.—FOURTH APPLICATION OF PRESSURE TO THE BREECH. THE INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST THE INTERNAL PRESSURE IN THOUSANDS OF POUNDS PER SQUARE INCH.

The result of the initial application of pressure to the muzzle is shown in Fig. 8. As in Fig. 5, results are plotted on two scales, a larger scale for the points before pronounced set occurred, and a scale five times smaller showing set. Just as in the case of the breech, the stress-strain relation on the initial application was not even approximately linear, but the curve started with pronounced curvature, passing into the region of flow without abrupt change of direction.

The diameters of the muzzle were 5.3 in. (13.5 cm.) outside, and 2.6 in. (6.6 cm.) inside. Applying computations similar to those for the breech, we find that the longitudinal strain is a shortening of 6.0×10^{-4} for 100,000 lb. per sq. in., that the theoretical elastic increase of diameter is 0.0111 in. (0.28 mm.) per 100,000 lb., and that the theoretical elastic limit, on the maximum stress basis, is 37,000 lb. (2600 kg. per sq. cm.). The maximum stress applied was 78,000 lb. The rate of recovery after release of pressure was 0.0119 in. (0.3 mm.) per 100,000 lb. per sq. in., much more nearly the theoretical rate than was shown by the thicker

[7] *Phys. Rev.* (1912) **34**, 11.

breech, in spite of the fact that the set was relatively and absolutely greater, 0.0767 in. (1.95 mm.) against 0.0530 in. (1.35 mm.).

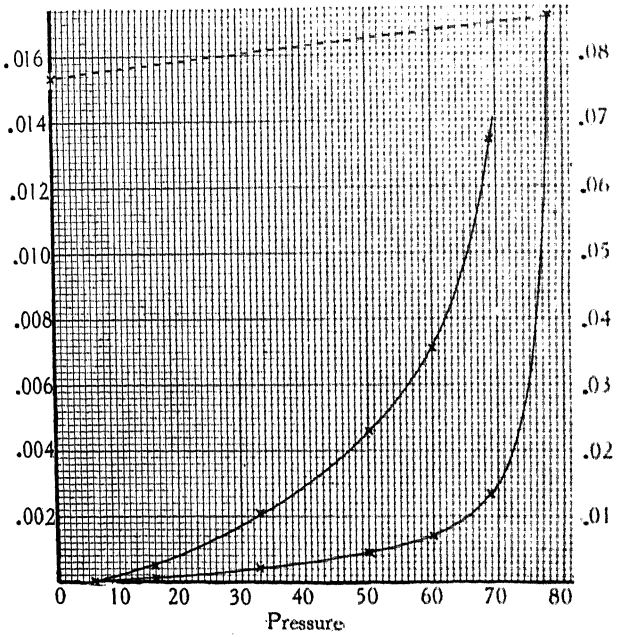


FIG. 8.—FIRST APPLICATION OF PRESSURE TO MUZZLE. INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST INTERNAL PRESSURE IN THOUSANDS OF POUNDS PER SQUARE INCH. RESULTS ARE SHOWN ON TWO SCALES; LEFT-HAND SCALE APPLIES TO UPPER CURVE, WHICH SHOWS STRAIN BEFORE PRONOUNCED FLOW HAS BEGUN, AND RIGHT-HAND SCALE APPLIES TO LOWER, WHICH SHOWS STRAIN DURING STAGES BOTH OF ELASTIC YIELD AND OF FLOW.

The result of the second application of pressure to the muzzle is shown in Fig. 9. The initial relation between stress and strain is linear within the limits of error of measurement, with a slope of 0.0106 in. (0.27 mm.) per 100,000 lb. The agreement with the calculated value is probably within the limits of error of the values assumed for the elastic constants. This linear relation is in striking contrast with the curvature shown in Fig. 5, taken under corresponding conditions at the breech. This agrees with all my previous experience that, after flow, equilibrium is attained much more rapidly in small than in large masses of metal, and that accommodation effects are always much less prominent. Briefly, the explanation of this is that in the smaller mass of metal there is less room to set up those internal stresses and inhomogeneities, the releasing of which causes the accommodation effects.

The previous pressure maximum of 78,000 lb. was slightly exceeded on the second application, pressure being pushed to 82,000 lb. The slight additional set of 0.0039 in. (0.1 mm.) on the second application was almost entirely produced by this excess pressure. On release of pressure, there were pronounced hysteresis effects, doubtless the result of the

slight additional flow produced by the excess 4000 lb. The total recovery on release was at the same average rate as the linear rate on application of pressure, namely 0.106 in. (2.7 mm.) per 100,000 lb. per sq. in.

After completion of the stretching, the bore was measured at the Navy

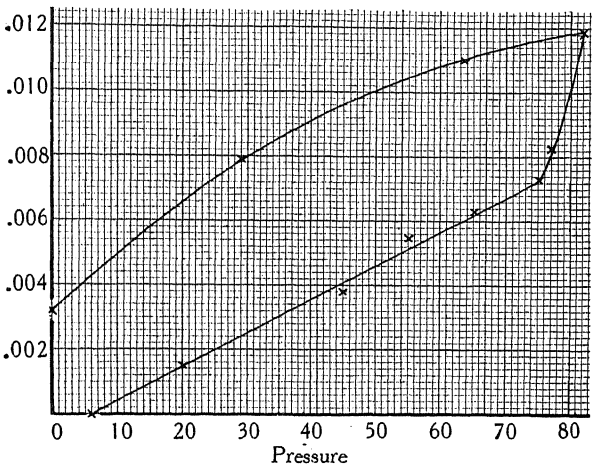


FIG. 9.—SECOND APPLICATION OF PRESSURE TO THE MUZZLE. THE INCREASE OF OUTSIDE DIAMETER (ORDINATE) IS SHOWN IN INCHES AGAINST THE INTERNAL PRESSURE IN THOUSANDS OF POUNDS PER SQUARE INCH.

Yard. Fig. 10 shows the internal permanent stretch at various points of the bore. The minimum at 33 in. corresponds to the transition from breech to muzzle. With the experience gained from this first trial it would evidently be possible to improve the position of the packing plugs so that the

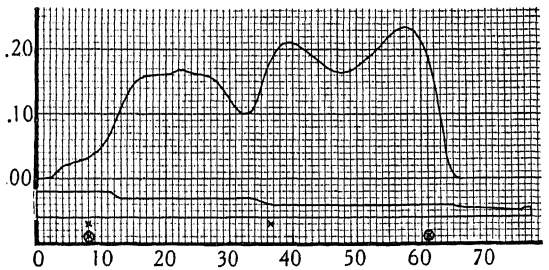


FIG. 10.—TOTAL INTERNAL STRETCH AFTER TREATMENT, IN INCHES (ORDINATE) AS FUNCTION OF POSITION, IN INCHES, ON AXIS OF GUN (ABSCISSA). CROSSES SHOW POSITION OF PACKING DURING APPLICATIONS OF PRESSURE TO BREECH ALONE, AND CROSSES IN CIRCLES POSITION OF PACKING DURING APPLICATION OF PRESSURE TO BOTH BREECH AND MUZZLE.

stretch of breech and muzzle would join each other continuously. The minimum at 48 in., on the other hand, must have been an intrinsic irregularity due to a local hardness in the forging. However, the stretch at all points of the bore was sufficiently great so that local irregularities had no bad effect, as shown by the final firing tests.

From a comparison of the final outside and inside dimensions, some idea can be gained as to whether there was any permanent change of density of the metal. At the center of the breech section, the computed metal added to the outside of the cylinder agreed with that taken from the inside to within 0.7 per cent. but at the muzzle the agreement was only within 14 per cent. However, the accuracy of the computation at the muzzle is not high because of the inhomogeneity of the metal, and, in particular, the possibility must be recognized that the figure did not remain circular; not enough measurements were made to be sure of this point. Within the limits of error, there was no great change of density. It is a result of my previous experience that hydrostatic pressure, as such, produces no permanent change of density, unless the metal has actual pores. Under such conditions of strain as were employed here, the density shows a slight tendency to decrease, if anything.

Summary

1. With regard to gun fabrication, it has been demonstrated by actual construction and firing tests that it is possible to make a gun from a single forging, producing the required distribution of internal stresses by a preliminary application of hydrostatic pressure so high as to strain the material considerably beyond its yield point. The great simplicity of construction by this method leads to the expectation of important economies of time and money if quantity production should be attempted.

2. The technique of controlling the pressures required, which are of the order of 100,000 lb. per sq. in. (7030 kg. per sq. cm.), has been described as applied to the experimental gun. The essence of the technique is a packing which automatically becomes tighter at higher pressures. There is no reason to think that the technique should not be successfully applied on a commercial scale.

3. The behavior of the hollow cylinders composing the gun, when stretched by heavy internal pressure, has been described. Such cylinders flow and receive permanent set under pressures which may be about twice the elastic limit computed according to the simple theories. After once stretching, the cylinder receives little or no further permanent set up to the previous pressure maximum. Within this range of pressure, the cylinder behaves in a manner approaching that of perfect elasticity, but with very marked disturbances, of which hysteresis and accommodation effects are the most prominent. These disturbances tend to disappear with time. The approach to perfectly elastic behavior is much closer for thin than for thick cylinders. A valid theory of the stress-strain relations under such conditions is much to be desired, but has not yet been formulated.

DISCUSSION OF THIS PAPER IS INVITED. It should preferably be presented in person at the New York Meeting, Feb. 16 to 19, 1920, when an abstract of the paper will be read. If this is impossible, discussion in writing may be sent to the Editor, American Institute of Mining and Metallurgical Engineers, 29 West 39th Street, New York, N. Y., for presentation by the Secretary or other representative of its author. Unless special arrangement is made the discussion of this paper will close Apr. 1, 1920. Any discussion offered thereafter should preferably be in the form of a new paper.

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FURTHER MEASUREMENTS OF THE EFFECT OF PRESSURE ON RESISTANCE

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Communicated August 22, 1920

In a previous paper[1] data for the effect of pressures up to 12000 kg/cm^2 on the resistance of 22 metals were given. It has now been possible to extend the results to 18 more elements, and 6 alloys. The extension has been made possible by two changes in the technique. In the first place, by a change in the method of leading electrical connections into the pressure chamber it has been possible to replace the previous method of measuring resistance with a Carey Foster bridge by a potentiometer method. This makes it possible to measure accurately specimens whose total resistance is very low, and removes the restriction that the specimen must be in the form of a fine wire. In the second place, by a modification in the design of the apparatus, it has been possible to considerably extend the temperature range. The results now cover a range from atmospheric to 12000 kg. pressure, and an extreme temperature range from 0° to 275° C.

In selecting the substances to be measured over this increased range I have paid particular attention to the matter of liquid metals. Previous to this, the effect of pressure on both the liquid and solid state was not known for a single metal. The resistance of metals in the liquid state would seem to be particularly worthy of study, because here the crystalline structure introduces no complications. Six elements have now been investigated in the liquid and the solid states. Furthermore, I have endeavored particularly to investigate some of the more unusual elements, in the expectation that elements from unusual parts of the periodic table might show new types of behavior. This attempt has been rewarded by the discovery of three more elements whose pressure coefficient of resistance is positive; bismuth and antimony were the only ones known previously.

ments on them had been already made for another purpose. The composition of the alloys is as follows:

Hoskins Mfg. Co.	Chromel A	Ni 80%, Cr 20%.
	Chromel B	Ni 85%, Cr 15%.
	Chromel C	Ni 64%, Cr 11%, Fe 25%.
Electrical Alloy Co.	Comet	Ni x%, Cr y%, Fe z%.
Driver Harris Co.	Therlo	Al 2%, Mn 13%, Cu 85 (this is like Manganin).
	No. 192 Alloy	Ni 30%, Cr 2%, Fe 68%.

Only a very rough summary of the principle results of the measurements can be attempted here. The results will be published in full detail elsewhere. In the table are shown the average pressure coefficients to 12000 kg., and also the initial coefficients at atmospheric pressure. The numerical values of the table may be supplemented by the following remarks on various significant aspects of behavior.

TABLE

EFFECT OF PRESSURE ON RESISTANCE

Substance	Mean Pressure Coefficient, 0–12000 kg.	Instantaneous Pressure Coefficient at 0 kg.	Substance	Mean Pressure Coefficient, 0–12000 kg.	Instantaneous Pressure Coefficient at 0 kg.
Li, solid, 0°	+0.0$_5$772	+0.0$_5$68	Bi, liquid, 275°	−0.0$_4$101c	−0.0$_4$123
Li, liquid, 240°	+0.0$_5$93	+0.0$_5$93	As, 0°	−0.0$_5$33	.....
Na, solid, 0°	−0.0$_4$345	−0.0$_4$663	W, 0°	−0.0$_5$135	−0.0$_5$143
Na, liquid, 200°	−0.0$_4$436	−0.0$_4$922	La, 0°	−0.0$_5$331	−0.0$_5$39
K, solid, 25°	−0.0$_4$604	−0.0$_5$186	Nd, 0°	−0.0$_5$213	−0.0$_5$238
K, liquid, 165°	−0.0$_4$809a	−0.0$_5$168	Carbon, amorphous, 0°	−0.0$_4$100	−0.0$_4$118
Mg, 0°	−0.0$_5$408	−0.0$_5$447	Carbon, graphite, 0°	+0.0$_5$47	+0.0$_5$77
Ca, 0°	+0.0$_4$106	+0.0$_4$129	Si, 0°	−0.0$_4$117	.....
Sr, 0°	+0.0$_4$680	+0.0$_4$502	Black phosphorus, 0°	−0.0$_4$81	−0.0$_5$200
Hg, solid, 0°	−0.0$_4$236b	.....	Chromel A, 0°	−0.0$_4$134	.....
Hg, liquid, 25°	−0.0$_4$219	0.0$_4$334	Chromel B, 0°	−0.0$_4$169	.....
Ga, liquid, 30°	−0.0$_5$531	−0.0$_5$640	Chromel C, 0°	−0.0$_5$427	.....
Ga, solid, 0°	−0.0$_5$247	.....	Comet, 0°	−0.0$_5$241	−0.0$_5$263
Ti, 0°	±0.0$_5$1??	.....	Therlo, 0°	−0.0$_5$228	−0.0$_5$236
Zr, 0°	−0.0$_5$40	−0.0$_5$40	No. 193 alloy, 94°	−0.0$_5$179	.....

a Average 0–9000 kg.
b Average 7640–12000 kg.
c Average 0–7000 kg.

With regard to purity, Ga was prepared under the direction of Professor T. W. Richards for atomic weight work, and had less than 0.01% impurity. The Na, K, Mg, Hg, Bi, W, and black phosphorus were also of high purity. The Ca contained about 0.1% impurity, and the impurity in the Li and Sr was of the order of 1%. The Ti and Zr were known to be impure with 1.8% and 0.6% of W respectively; the impurity

La, and Nd were considerably impure. The graphite was the best Acheson graphite, but the results were not reproducible. Similarly results with Si were not reproducible. All that can be expected of C and Si is the order of magnitude of the effect.

Normal Solids.—The substances with negative pressure coefficients of resistance are Na, K, Mg, Hg, Ga, Ti, Zr, As, W, La, Nd, Si, and black phosphorus. Mg and W were previously measured. It is now possible to give better values because of increased purity of the specimens available. La and Nd are the first metals in the rare earth group whose pressure coefficients have been measured; they show no novel features. Ti and Zr are also from a new region of the periodic table. The interesting feature of their behavior is the extreme smallness of the coefficient. Hg has not been previously measured in the solid state; its coefficient is somewhat greater than that of the liquid. Abnormal results were expected for gallium, because it expands when it freezes, but it was found instead to be quite normal. Arsenic might be anticipated to be abnormal because of its position in the periodic table relative to bismuth and antimony, but it turns out to be normal. Silicon, a non-metallic element, decreases in resistance, as is normal for metals, but the pressure coefficient becomes larger with increasing pressure and the temperature coefficient may reverse in sign at high pressures, both of which are abnormal features. Black phosphorus, also non-metallic, is remarkable for the very large size of the effect, the resistance decreasing under 12000 kg. to about 3% of its initial value. The relative coefficient, however, does not change so much as it does for some metals. Na and K are the first alkali metals whose pressure coefficients have been measured. They are remarkable for the largeness of the effect, which is larger than for any other metals as yet measured. Na decreases 40% and K 70% in resistance under 12000 kg. The pressure coefficient of these metals decreases greatly with increasing pressure and increases with increasing temperature, and the temperature coefficient decreases with increasing pressure. The metals previously measured have shown relatively little change in these coefficients.

Abnormal Solids.—Three new elements have been found whose resistance increases under pressure; these are Li, Ca, and Sr. This was a great surprise because all of these metals are highly compressible. With the single exception of the variation with pressure of the pressure coefficient of strontium, the behavior of these three metals is like that of Bi and Sb in that the instantaneous pressure coefficient increases with increasing pressure and decreases with increasing temperature, and the temperature coefficient falls with rising pressure.

Relative behavior of Resistance of Solid and Liquid.—The pressure coefficient of liquid bismuth is found to be negative and normal, although

of crystalline structure in determining the variations of resistance. On the other hand the coefficient of lithium is abnormal in being positive in both the liquid and solid states. (The melting curve of Li was measured under pressure and found to be normal in that the solid expands on melting.) The magnitude of the coefficient of the solid is less than that of the liquid. Gallium is normal in the solid as well as in the liquid, and the coefficient of the liquid is much larger than that of the solid. The coefficient of liquid mercury is slightly less than that of solid mercury. The coefficients of liquid sodium and potassium are less than those of the solids, but by only small amounts. The relative decrease in the coefficients of these solids with pressure may be greater than the decrease of the liquid. Liquid potassium has an abnormal change in the sign of the variation of temperature coefficient with pressure and the pressure coefficient with temperature.

All of the six metals measured in the solid and liquid state agreed in showing a relatively small change in the ratio of the resistance of liquid to solid along the melting curve from low to high pressure. Thus the change in the ratio of the resistance of liquid to solid potassium was from 1.56 to 1.55 under a pressure increase of 9700 kg. This pressure is sufficient to decrease the difference of volume between liquid and solid to 0.31 of its initial value. It seems to be universally true that the temperature coefficient of the liquid is less than that of the solid, and the change of resistance on melting is in the direction of the change of volume.

Theoretical Implications.—The following remarks are only two of many that might be suggested by the data.

It is probable, because of the peculiar nature of the atomic structure of lithium and the fact that its pressure coefficient of resistance is positive, that the picture of the mechanism of electrical conduction given by Wien and Lindemann as a space lattice of electrons sliding in the channels of a space lattice of atoms may have much of truth for this particular element.

The new evidence now at hand does not make it necessary to modify the former point of view[2] that for most elements the most important single factor in determining the variations of electrical resistance is the amplitude of atomic vibration.

This investigation was assisted in large part by a generous grant from the Rumford Fund of the American Academy of Arts and Sciences.

[1] Bridgman, P. W., *Proc. Amer. Acad., Boston*, **52**, 1917, (573–646).

[2] Bridgman, P. W., *Physic. Rev., Ithaca, N. Y.*, **9**, 1917 (269–289).

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THE ELECTRICAL RESISTANCE OF METALS.

BY P. W. BRIDGMAN.

SYNOPSIS.

Electrical Resistance of Eighteen Elements.—The paper contains a brief summary of an extensive series of measurements which are to be published in detail elsewhere made to determine the *effec t of pressures up to* 12000 *kg. per sq. cm. and of temperatures from* 0° *to* 275° *C.* on the resistance of *lithium, sodium, potassium, gallium, bismuth, mercury, calcium, strontium, magnesium, titanium, zirconium, arsenic, tungsten, lanthanum, neodymium, carbon (amorphous and graphitic), silicon, and black phosphorus.* The data for tungsten and magnesium are improvements on data previously published; the data for the other substances are new. The first six of these elements were studied in both the liquid and the solid states. The pressure coefficients of solid calcium, solid strontium, and both solid and liquid lithium are positive; the coefficient of bismuth is positive in the solid state, but negative in the liquid.

Modified Electron Theory of Metallic Conduction.—A previous theoretical discussion of measurements of the effect of pressure on resistance suggested most strongly that in metallic conduction the electrons pass through the substance of the atoms, and that the mechanism by which resistance is produced is *intimately connected with the amplitude of atomic vibration.* This view is here given quantitative form. The classical expression for conductivity, $\sigma = (e^2/2m)(nl/v)$, is retained; the number of free electrons is supposed to remain constant, their velocity is taken to be that of a gas particle of the same mass and temperature, and their mean free path is supposed to be many times the distance between atomic centers. The variations of path are then computed in terms of the variations of amplitude, and thus the variations of resistance are obtained and *checked with experimental results.* It is shown that the theory in this form explains Ohm's law, gives the correct temperature coefficient and the most important part of the pressure coefficient, avoids the difficulty of the classical theory with reference to specific heats, indicates a vanishing resistance at low temperatures, leaving open the possibility of super-conductivity, and retains the classical expression for the Wiedemann-Franz ratio. Besides these quantitative checks, the theory is shown to be entirely consistent qualitatively with all the new data; in fact, many of these new results, particularly the effect of pressure and temperature on the relative resistance of solid and liquid, seem to demand uniquely this conception of metallic conduction.

IN a forthcoming number of the Proceedings of the American Academy I shall give the results of measurements of the effect of pressure and temperature on the resistance of 18 elements and several alloys. This is additional to my previous results for 22 elements. The numerical data will be briefly summarized in the Proceedings of the National Academy. In a previous paper in this journal[1] I drew certain inferences

with regard to the mechanism of electrical conduction from the previous data for 22 substances. In this paper I desire to extend this work in the light of the new data now available.

It will pay to briefly indicate the extent of the new data; the numerical results will be referred to in the following as the need arises. Previous to these measurements there were data for the effect of pressure on the resistance of no metal in both the liquid and the solid state, and the data were known for only one liquid metal, mercury. I have now obtained results for the variation of resistance under both pressure and temperature of the following six metals in both the liquid and the solid states: mercury, lithium, sodium, potassium, gallium, and bismuth. Previously none of the alkali or alkali earth metals had been measured; it is just these for which the largest pressure effects would be expected. I now have the data for lithium, sodium, potassium, calcium, and strontium. The effect of pressure was not known on any of the rare earth metals. I now have the data for La and Nd. The complete list of elements covered by the new work is: Li, Na, K, Mg, Ca, Sr, Hg, Ga, Ti, Zr, Bi, As, W, La, Nd, C, I, and P (black). Perhaps the most striking of the new results are as follows. Three more metals have been added to the list of those whose resistance increases with increasing pressure; these are Li, Ca, and Sr. Bi and Sb were the only ones previously known. Of these Li was a particular surprise, because its compressibility is so high. The resistance of liquid as well as solid Li increases under pressure. The resistance of liquid Bi, on the other hand, decreases under pressure, although that of the solid increases. I expected that the resistance of gallium would also increase under pressure, because this substance is abnormal in expanding on freezing, but its resistance decreases normally with pressure in both the solid and the liquid states. The effects of pressure on the resistance of Na and K are much larger than for any other metals, Na decreasing 40 per cent. in resistance under 12,000 kg., and K decreasing by 70 per cent. The decreases of these metals are insignificant compared with that of black phosphorus, however, which decreases to 3 per cent. of its initial resistance under the same pressure. The change is entirely reversible. The pressure coefficient of carbon has opposite signs in the amorphous and graphitic phases.

In my previous theoretical paper I directed especial emphasis to one fact brought out by the previous measurements, namely that the most important single factor in affecting the resistance of a metal is without doubt the amplitude of vibrations of the atoms. It turned out that the relative change of resistance under a change of either temperature or pressure was equal approximately to twice the corresponding change

of amplitude of atomic vibration. The relation was fairly accurate for all metals with regard to the temperature coefficient (which is nearly the same for all metals and equal to the reciprocal of the absolute temperature), and was not so exact for changes of pressure, but nevertheless was somewhat more accurate than any other relation previously proposed for the pressure change. This fact seemed to me to indicate that the mechanism of conduction was by a passage of electrons from atom to atom through the substance of the atom itself. The atom is to be thought of as normally offering no resistance to the passage of the electron (super-conductivity at absolute zero), but resistance may be encountered in passing from atom to atom. The assumption of paths within the atom which are resistanceless need occasion no alarm in these days of non-radiating quantum orbits. In fact there may be an intimate connection between the two. I had called this theory the "gap" theory of resistance. Not only the quantitative fact that the resistance varies as the square of the atomic amplitude, but a large number of qualitative facts also, were in accord with this point of view. These qualitative facts were many of them brought into line by the conception that the "gap" may function in two ways. At large mean distances of separation of the atoms it may happen that passage of electrons from atom to atom is made easier by temperature agitation of unusual violence, which brings the surfaces of the atoms closer together than normal during part of their vibration, whereas at small mean distances of separation, the passage of electrons is on the average hindered by temperature agitation. Except for the deduction of the expressions for the variation of atomic amplitude with temperature and pressure, the theory as hitherto expounded was qualitative rather than quantitative. In particular, I did not attempt to give any detailed picture of the way in which the gaps between atoms might offer resistance to the passage of electrons, or what the character of the resistance might be. The theory as previously given also made no attempt to explain the Wiedemann-Franz ratio, although I pointed out that an explanation was not inconsistent with the elements of the theory.

It is now possible to cast this point of view into quantitative form, at least as far as temperature variations of resistance go; the pressure changes cannot be so easily dealt with for a reason that will appear later.

In the first place it is interesting to observe that the proportionality of resistance to the square of the amplitude of atomic vibration holds also at low temperatures; the previous considerations were entirely confined to ordinary temperatures. It has been noticed by Grüneisen,[1]

[1] E. Grüneisen, Verh. D. Phys. Ges., 15, 186–200, 1913.

after an examination of the best data, that down to very low temperatures the quotient of resistance by absolute temperature is proportional to specific heat, the factor of proportionality being different for different metals. Let us compare this experimental variation of resistance with a variation as the square of the amplitude of atomic vibration at low temperatures. The specific heat formula which best fits the facts at low temperatures is that of Debye. This gives an energy content proportional to the fourth power of the absolute temperature, and of course a specific heat proportional to the third power, since the specific heat is obtained by differentiating the energy. We have, therefore, the expressions,

$$E = At^4 \qquad \text{and} \qquad C = 4At^3,$$

where E and C are the energy and the specific heat of the atom respectively. We may also express the energy of the atom in terms of its frequency and amplitude of vibration. This gives the equation

$$2\pi^2 m\nu^2\alpha^2 = At^4,$$

where α is the amplitude, and ν the frequency of atomic vibration. Now differentiate this expression logarithmically with respect to t, giving

$$\frac{2}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p = \frac{4}{\tau} - \frac{2}{\nu}\left(\frac{\partial\nu}{\partial\tau}\right)_p.$$

The value of $1/\nu(\partial\nu/\partial\tau)_p$ was found in the previous paper. Substituting this value gives

$$\frac{2}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p = \frac{4}{\tau} - 2\left(\frac{\partial v}{\partial\tau}\right)_p^2 \Big/ C_v\left(\frac{\partial v}{\partial p}\right)_\tau.$$

An examination of the previous deduction of $1/\nu(\partial\nu/\partial\tau)_p$ shows that the connection between temperature and energy did not enter, so that the same expression is valid at low as well as high temperatures. But now it is an empirical fact that at low temperatures the compressibility approaches a constant value, and that the ratio of the thermal expansion to the specific heat also approaches a constant value. Hence in the limit $(\partial v/\partial\tau)_p^2/C_v(\partial v/\partial p)_\tau$ becomes proportional to $(\partial v/\partial\tau)_p$, and hence vanishes. We have, therefore, at low temperatures,

$$\frac{2}{\alpha}\left(\frac{\partial\alpha}{\partial\tau}\right)_p = \frac{4}{\tau}.$$

At high temperatures $2/\alpha(\partial\alpha/\partial\tau)_p$ was also proportional to $1/t$, but the factor of proportionality was 1 instead of 4.

Now our previous empirical observation was that $2/\alpha(\partial\alpha/\partial\tau)_p$ gives the variation of resistance with temperature. Compare this with

Grüneisen's empirical observation. He has

$$R/t = BC,$$
$$R = BCt$$
$$= 4ABt^4,$$

where R is the resistance and B a constant. Hence

$$\frac{1}{R}\frac{dR}{dt} = 4/t,$$

which checks precisely with the value of twice the variation of atomic amplitude.

Although we have found a variation at high and low temperatures proportional to the variation of the square of the amplitude, we cannot set the resistance at all temperatures equal to a constant times the square of the amplitude (that is if Grüneisen's observation is correct) for the factor of proportionality changes on passing from low to high temperature. The relation of proportionality must therefore fail at some intermediate temperature.

Returning now to the task of making the "gap" theory more definite, we in the first place make specific the action of the gap in imparting resistance by picturing precisely the same sort of mechanism as that operating during a collision of the classical theory. There cannot be any doubt that the electron encounters difficulty in getting free from the atom when the atoms are separated from each other as in a gas, for there is a definite ionizing potential, which involves an amount of energy large in comparison with that ordinarily available in the form of temperature energy of agitation. It is also evident that in some way the electrons do get free from the atoms in the solid state, because the solid is conducting for any E.M.F., no matter how small, and at low temperatures its Ohmic resistance vanishes. This means that under certain conditions forces may act on the electron when in the act of passing from one atom to another, whereas while the electron is passing through the interior of the atom no forces act. During the action of a force between electron and atom, there is a chance for the transfer of energy from one to the other, so that we have a tendency to equipartition. In other words, the "gap" produces resistance by interfering with or terminating the free path of the electron, precisely as did the "collision" in the classical theory. The amount of interference with the free path will depend on the amplitude of vibration, and so the resistance will depend on the amplitude. Such a picture as this enables us to carry over immediately much of the analysis of the classical theory. For instance, the classical ex-

pression for the resistance at once holds, namely,

$$R = \frac{2m}{e^2} \frac{v}{nl}, \qquad (1)$$

where e is the charge on the electron, m the mass of the electron, n the number of electrons describing paths per cm.^{3}, l the mean free path of the electron, and v the undisturbed velocity of translation of the electron.

Ohm's law at once follows on the same basis as in the classical theory. Previously I had to leave Ohm's law unexplained, with only the remark that there was no inconsistency.

This picture of the mechanism of interference with the free path is so different physically from that of the classical theory, and yet gives such similar results when substituted into the mathematical expression, that it will pay to stop for a moment to inquire what is our justification for setting up so definite a picture. In particular, we may compare this picture with that of Wien,[1] who also has a free path mechanism of conduction and Ohm's law, but imagines the electrons interfered with in their flight by collisions with the centers of the atoms. Many facts are equally understandable from either point of view. There are a number however, which are more naturally explained by supposing that the interference encountered is in passing through the surface from one atom to the next. Many of these facts will be given later; I mention only the two most striking. In the first place it is a universal fact that if a metal changes form, as by melting, or by a polymorphic transition, the phase with the smaller volume has the smaller resistance. This holds for all known normal meltings, in which the liquid has the larger volume, and also holds for the abnormal meltings of Bi, Sb, and Ga, in which the liquid has the smaller volume, and also the smaller resistance. It holds also for the normal polymorphic transitions of Zn and Ni, and for the abnormal transition of Tl, in which the high temperature phase has the smaller volume. Now this is difficult to understand from Wien's point of view, for it would seem that in the phase with the smaller volume there must be more chance of collision with the atomic centers, and so a higher resistance. The difficulty cannot be turned by supposing that the energy of temperature agitation is different in the two phases, for the specific heat of liquid bismuth is greater than that of the solid, and therefore in the liquid the atoms have more chance of terminating the free path both because they are more numerous, and because their amplitude of temperature agitation is greater, so that they effectively cover more territory. On the other hand, the fact that the resistance of the phase

[1] W. Wien, Columbia Lectures, 1913, 29–48.

with the smaller volume is the smaller is most naturally explained from the "gap" point of view simply by the observation that the atoms are closer together, and the electrons find it easier to pass from one to another. Another fact not readily understandable from Wien's point of view is that the temperature coefficient of resistance of the liquid is nearly always less than that of the solid. In some cases it may be very much less, or may even be negative, instead of positive. Now the increased violence of temperature agitation in the liquid, as shown by the higher specific heat, would seem to demand a higher temperature coefficient, according to Wien's view. There is a most natural explanation in terms of the gap theory, as has been explained in the preceding paper, or as will be elaborated further in the following.

So much for the mechanism by which resistance is produced, and the explanation of Ohm's law. To get further, we have to know the precise manner of variation of n, l, and v with temperature and pressure. The classical theory supposed that v was the value given by the equipartition of energy, treating the electron as a gas particle, that l was at least of the order of magnitude of the distance between atomic centers, and n could look out for itself, being determined by the necessities of the case. The weaknesses of the old theory are well known. One of the most serious is that the n needed to give the observed values of specific resistance is of the order of magnitude of the number of atoms itself, or even may be considerably in excess, which leads to the insuperable difficulty of the specific heat. An n of the same order of magnitude was indicated by the application of the theory to the optical theory of metals. Many attempts have been made to avoid this difficulty, but as yet without success. Nearly all attempts at replacing the classical theory have failed in the endeavor to give even an approximate explanation of the Wiedemann-Franz ratio. In order that the thermal conductivity of a metal shall have its high value, and in order that the Wiedemann-Franz ratio may have approximately its experimental value, it seems to be necessary to suppose not only that temperature energy is carried by the electrons, but that the amount so carried is precisely the amount which would be carried if the energy of the electrons were the equipartition energy on the old classical basis.

Apparently the most promising attempt at another explanation of the Wiedemann-Franz ratio is the recent theory of Borelius,[1] which does give a result of approximately the right magnitude. But although his explanation may be mathematically satisfying, I do not think that it can be considered satisfactory physically. His explanation is on the

[1] G. Borelius, Ann. Phys., 57, 278–286, 1918.

basis of the Debye theory of heat conduction.[1] Debye's theory is that heat is conducted by elastic waves, which are dissipated by atomic irregularities. A quantity analogous to the mean free path may be defined in terms of the rate of dissipation, so that the higher the rate of dissipation the shorter the equivalent free path, and the less the conductivity. Debye has applied this theory to insulators, like rock salt, and has been able to account for the experimental fact that the conductivity varies inversely as the absolute temperature. Borelius has taken over this theory for metallic conduction, by means of the assumption that the amount of energy dissipated at each atom as the elastic wave passes over it is equal to the ratio of the thermal energy of the atom to that of the electron. This gives a thermal conductivity of the right order of magnitude. In combination with his theory of electric conduction he gets a Wiedemann-Franz ratio of approximately the right magnitude, and with the right dependence on temperature. But he has neglected the dissipation of the elastic waves due to the atoms. If Debye's analysis is correct, this should be present in the metal as well as in an insulator, and is very much larger than the dissipation supposed by Borelius. Hence, taking account of the neglected atomic dissipation, the thermal conductivity of a metal would turn out to be actually less than that of an insulator, for there is dissipation not only by the atoms but also by the electrons.

Compared with the classical conception of conduction as performed by a swarm of electrons playing in the free spaces between the atoms, the view at which we have arrived of conduction as performed by electrons passing freely through the substance of the atoms places us in a much more advantageous position, for it allows the possibility of very long free paths (in fact at absolute zero there is no resistance to the motion and the paths may be indefinitely long), and hence enables us to get along with many fewer electrons. In this way the specific heat difficulty may be avoided. But in order to account for the facts of thermal conduction, it seems necessary to take over the classical idea that the electrons are moving with the energy of gas particles at the same temperature.

The theory developed here proceeds on the following assumptions. We take over the classical expression (I) for resistance in terms of n, l, and v. We suppose that v is the same as that given by the classical equipartition theory, and we suppose l large enough to avoid the specific heat difficulty by allowing a small value of n. We try to deduce from our fundamental expression the variation of resistance with temperature

[1] P. Debye, Wolfskehlstiftung Vorträge, B. G. Teubner, 1914, 17–60.

and pressure in terms of the variations of v, which are given by the classical expression, and the variations of l, which we get from our picture of the electrons jumping from atom to atom across a region capable of exercising interference with the path. The quantity n we suppose to stay constant. One reason for this supposition is that we do not need to assume any variation in order to account for the facts. However, it does not seem unplausible that n should stay approximately constant. As temperature is increased, the tendency to an increased n due to the increased chance of getting an electron out of an atom by increasing violence of collision is counterbalanced by the increasing difficulty of getting the electron out of the atom because of the increased distance of separation of atomic centers. Or again, it may be that the number of migrating electrons is determined by a sort of spontaneous atomic disintegration in the outer part of the atomic structure, over which changes of temperature or of pressure can have no control.

There is evidence as to the magnitude of n given by optical theories of metals. We shall for the present merely disregard this. We are much more justified in doing this now than we would have been several years ago, for quantum theory has made it exceedingly uncertain whether we are justified in keeping our old model of a vibrating electron as a source of light. Quantum theory has shown,[1] for example, that the success of the electron in giving the classical expression for the Zeeman separation was due to a quite accidental cancelling out of the factor h from the result, and that the factor h will not so conveniently cancel out in treating certain other phenomena, as the Stark effect. Furthermore, the number of electrons demanded by optical theory must now seem impossibly high in the light of our knowledge of the structure of the atom, so that we are probably justified in disregarding the line of attack from the optical side until quantum theory has become more developed.

Concerning our assumption of the equipartition value for v, putting it equal to $\sqrt{2(\kappa\tau/m)}$, there cannot be much question at moderate temperatures, so long as n is small enough to avoid the specific heat difficulty, but there may be question as to what the limit of temperature is to be. It is possible that the classical expression for the energy may hold to lower temperatures for the electron than for the atom. Hydrogen or helium at low temperatures in the gaseous condition in contact with the solid walls of the container continues to have the classical energy, although this is no longer the equipartition energy as compared with the atoms of the solid walls. However, the classical expression cannot continue to hold indefinitely to extremely low temperatures, for even a few

[1] A. Sommerfeld, Atombau und Spektrallinien, Vieweg, 1919, 422–440.

electrons with the classical energy would ultimately make trouble with the specific heat. We will not concern ourselves further with the situation at extremely low temperatures except to remark that the assumptions of this theory will have to be modified, and to indicate that such a modification is not at all impossible. For instance, the electron in coming from the atom, leaves behind it a positively charged ion. As the electron wanders through the metal it must at some time come again in contact with an ion, and may recombine with it. Throughout the metal, therefore, there is going on a continuous process of emission of electrons by the atoms and reabsorption. Now the mechanism of the ejection of the electron by the atom within the solid is something which we do not understand, but it is not unlikely that it is determined from within the atom, and is not greatly affected by outside conditions, at least as far as the velocity of emission is concerned. The electron may, therefore, be expelled with a definite velocity independent of temperature. It then travels from atom to atom, and is jostled about, until it ultimately acquires the equipartition energy. The time required to accomplish equipartition may well be less the greater the violence of agitation. Presently, the electron recombines with an ion. At low temperatures, because of the feebleness of temperature agitation, it may be that the electron is absorbed before it has acquired the equipartition energy, or that it has possessed this energy for only a relatively short time. The specific heat difficulty will not then appear, and the conductivity will be even higher than that corresponding to Grüneisen's empirical observation, because the mean velocity will not decrease so rapidly with decreasing temperature. And it is of course a fact that some metals show superconductivity at extremely low temperatures, and that superconductivity is not covered by Grüneisen's formula.

So much for the assumptions with regard to v and n. Now for a deduction of the variation of l, the mean free path.

There is a point implied in our assumption of a long free path which may detain us for a moment. We have pictured the electron as passing through the substance of many atoms before its path is arrested. Now in a cubic crystal this means that the electronic paths may be confined to three directions mutually at right angles, along the crystalline axes. The classical deduction for the expression for conductivity assumes of course that the directions of the paths are distributed at random throughout space. Is a specialized distribution in only three directions consistent with the known fact that the resistance of a cubic crystal is independent of the direction? A simple analysis immediately shows that there is no inconsistency here. Imagine the applied electric force making

the angles α, β, and γ with the crystal axes, and find the contribution made to the conductivity by the electrons moving along the X axis. The component of force along this axis is $E \cos \alpha$, so that the velocity imparted to the electron is smaller by the factor $\cos \alpha$ than it would be if the force were along the axis. And the component of this velocity in the direction of the force is further diminished by the factor $\cos \alpha$, so that the total contribution of the electrons moving along the X axis is diminished by the factor $\cos^2 \alpha$. Similarly the electrons moving along the other two axes contribute to the conductivity terms equal to $\cos^2 \beta$ and $\cos^2 \gamma$. The sum of the three terms is 1, which is thus independent of direction.

On the other hand, there is no necessity in supposing that a single free path is straight; the electrons may perform Virginia reels about the nuclei of the atoms in quantum orbits. Something of this sort probably has of necessity to take place in non-cubic crystals.

We return to the question of the variation of l. For the moment we consider that the solid is maintained at constant volume. As temperature is increased, the amplitude of vibration is increased, and it may be that during part of the vibration the atoms are so far separated that the electron cannot pass. That is, when the atoms are in vibration, there is a certain chance that the free path of the electron may be terminated in the passage from one atom to the next. This chance is a function both of the amplitude of atomic vibration, and of the mean distance of separation of atomic centers. Call β the chance that the path will be terminated, r the mean distance of separation of atomic centers and α the amplitude of atomic vibration. Then we may expand the unknown function in powers of α and write

$$\beta = f(r, 0) + \alpha \frac{\partial f(r, 0)}{\partial \alpha},$$

provided that α is small. α may be calculated, and it turns out that for ordinary temperatures α is a small fraction of r. Now it is our fundamental assumption that when the atoms are at rest no resistance is encountered in passing from atom to atom, provided that the distance of separation of atomic centers is not too great, as we suppose it is not for a solid. This means that $f(r, 0) = 0$, and we may write

$$\beta = \alpha \frac{\partial f(r, 0)}{\partial \alpha}.$$

That is, so long as the volume is kept constant, the chance that the path will be terminated in passing from atom to atom is proportional to α. In unit distance the chance that the path will be terminated is equal to β

multiplied by the number of atoms in unit length, again giving a constant times α. Now the probability definition of the mean free path is merely the reciprocal of the chance that the path will be terminated in unit distance, so that we have at once

$$l = \text{Const } \alpha.$$

To compute the variation of l at constant volume it is sufficient to calculate the variation of α at constant volume.

Now the variation of α was already computed in the previous paper. The expressions there given were for the variation of α with pressure and temperature, but of course from these derivatives the derivative at constant volume may at once be found if we know the compressibility and thermal expansion of the substance.

The computation of the change of amplitude is the only place in the theory into which the quantum hypothesis explicitly enters. The assumptions at the basis of the computation were these. The energy of the atom is the classical amount, $\kappa\tau$ (so that the deduction does not hold for low temperatures), the frequency is a function of volume only (the forces on the atoms are on the average a function of volume only), and the entropy of the atom is the same as the entropy of an ideal linear oscillator at the same temperature, which by quantum considerations is shown to be a function of τ/ν only.

For convenience of reference the values previously found are reproduced here.

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial p}\right)_\tau = -\left(\frac{\partial v}{\partial \tau}\right)_p \Big/ C_v,$$

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial \tau}\right)_p = \frac{1}{2\tau} - \left(\frac{\partial v}{\partial \tau}\right)_p^2 \Big/ C_v\left(\frac{\partial v}{\partial p}\right)_\tau.$$

The change of amplitude at constant volume may at once be found

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial \tau}\right)_v = \frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial \tau}\right)_p + \frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial p}\right)_\tau\left(\frac{\partial p}{\partial \tau}\right)_v.$$

But

$$\left(\frac{\partial p}{\partial \tau}\right)_v = -\left(\frac{\partial v}{\partial \tau}\right)_p \Big/ \left(\frac{\partial v}{\partial p}\right)_\tau.$$

Substituting this value above gives at once the simple result

$$\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial \tau}\right)_v = \frac{1}{2\tau}.$$

Now let us find the change of resistance at constant volume with

temperature. Our formula for the specific resistance is

$$R = \frac{2m^{1/2}(2\kappa)^{1/2}}{e^2 n}\frac{\tau^{1/2}}{l}$$

$$= \text{Const}\frac{\tau^{1/2}}{l}.$$

Differentiating this logarithmically gives

$$\frac{1}{R}\left(\frac{\partial R}{\partial \tau}\right)_v = \frac{1}{2\tau} - \frac{1}{l}\left(\frac{\partial l}{\partial \tau}\right)_v.$$

Using the value found for l in terms of α gives

$$\frac{1}{l}\left(\frac{\partial l}{\partial \tau}\right) = -\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial \tau}\right)_v,$$

and substituting this gives

$$\frac{1}{R}\left(\frac{\partial R}{\partial \tau}\right)_v = \frac{1}{\tau}.$$

That is, the temperature coefficient of resistance at constant volume is the reciprocal of the absolute temperature. This of course, is in accord with the experimental facts. In my preceeding theoretical paper I gave the values of $1/R(\partial R/\partial \tau)_v$. The difference between $1/R(\partial R/\partial \tau)_v$ and $1/R(\partial R/\partial \tau)_p$ is not large, but is in the direction to make $1/R(\partial R/\partial \tau)_v$ even more nearly equal to $1/\tau$ than $1/R(\partial R/\partial \tau)_p$.

The change from the point of view of the last paper is to be noticed. We previously thought of the change of α as the only significant feature, and noticed that $1/R(\partial R/\partial \tau)_v$ was equal to $2/\alpha(\partial \alpha/\partial \tau)_v$. We did not see any particular reason why the change of resistance should be proportional to twice the change of α, that is, why the resistance should be proportional to the square of the amplitude, although we advanced reasons which made it seem not improbable. Our present expression for R demands that we analyze the change of resistance into two effects; one is a temperature effect, due to the term $\tau^{1/2}$, and the other is an effect due to the change of l, which involves the change of α. Now it turns out that the change of l with α, which again changes with temperature, is of such a nature that the sum of the two effects is as before exactly equal to twice the change of α. Hence the previous analytical result stands, but our physical analysis is different.

We now let fall the condition that the volume be kept constant during the change, and consider the change of resistance with temperature at constant pressure, which is the coefficient usually directly determined by experiment. The formal work of differentiation of our fundamental

expression for resistance may be carried through as before. We encount difficulty in determining the variation of the mean free path with ter perature, for the condition no longer holds that the volume is constan and β, the probability of the termination of the path, can no longer b put equal to a constant times the amplitude, but the factor multiplyin the amplitude is an unknown function of the volume. I have not foun any universal assumption as to the dependence of β on the distance o separation of atomic centers which seems to be plausible, but it woul seem that β might vary in any way with the structure of the particula atom. For instance, it is conceivable that as the distance of separatio of atomic centers is increased the atoms acquire rotational movemen with respect to each other, so that parts of the atomic surfaces ar brought into opposition which are not so favorable for the passage o electrons. The magnitude of this effect will depend entirely on the struc ture of the particular atom. Or again, as the atoms are brought close to each other, the ease of passage will be affected by the deformation o the atom, and this again varies in an unknown way from element to element. The only fact about this unknown effect of changing distance between atomic centers which it seems fairly safe to assume as common to most elements is the sign; it is likely that as the atoms are brought closer together at constant amplitude the ease of passage is increased, and so the mean free path is increased.

The unknown effect of changing volume will evidently be much greater for those changes of volume relatively large compared with the change of amplitude. This means that the unknown effect will be much larger for changes of pressure than for changes of temperature. The magnitude of these changes was considered in the previous paper. It was there shown that the pressure coefficient of amplitude is from six to nine times the pressure coefficient of distance of atomic separation (linear compressibility), whereas the temperature coefficient of amplitude was from 50 to 650 times as great as the temperature coefficient of atomic separation (linear dilatation). In view of the largeness of this latter ratio, it would seem that we are justified for most substances in neglecting the effect as far as variations of temperature at constant pressure are concerned. We will, as a matter of fact, make this assumption. We then have

$$\frac{1}{l}\left(\frac{\partial l}{\partial \tau}\right)_p = -\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial \tau}\right)_p,$$

and analysis exactly like the preceding would give

$$\frac{1}{R}\left(\frac{\partial R}{\partial \tau}\right)_p = \frac{1}{\tau} - \left(\frac{\partial v}{\partial \tau}\right)^2 \Big/ C_v \left(\frac{\partial v}{\partial \phi}\right)$$

Now for all solid metals the second term is small compared with the first, and we may neglect it. We may now replace R, the specific resistance by ρ, the observed resistance (that is, the resistance of a piece of wire with fixed terminals), since the difference of the two coefficients is equal to the linear expansion, which may be neglected in comparison with $1/\tau$, and obtain as our final approximate result

$$\frac{1}{\rho}\left(\frac{\partial \rho}{\partial \tau}\right)_p = \frac{1}{\tau}.$$

This equation, of course, agrees with experimental fact. The usual temperature coefficients are always somewhat larger than $1/\tau$, which is the direction of variation which the above considerations would lead us to expect. I know of no theory which gives the departure of the temperature coefficient from $1/\tau$. Wien's theory is the only one which makes the attempt, and this cannot be regarded as successful. Of course the classical theory does not account for the temperature coefficient at all, but is driven to unplausible assumptions as to the variation of the free path with temperature in order to be consistent.

Now to find the pressure coefficient, we differentiate our expression for resistance with respect to pressure at constant temperature, getting

$$\frac{1}{R}\left(\frac{\partial R}{\partial p}\right)_\tau = -\frac{1}{l}\left(\frac{\partial l}{\partial p}\right)_\tau.$$

The only statement which we can make about $1/l(\partial l/\partial p)_\tau$ is that it is at least as large as $1/\alpha(\partial \alpha/\partial p)_\tau$, so that we expect the pressure coefficient of resistance to be at least as large numerically as $(\partial v/\partial \tau)_p/C_v$ (substituting the value found above for $1/\alpha(\partial \alpha/\partial p)_\tau$) and to be negative. In the previous paper it was shown that the pressure coefficient is given on an average for a large number of metals by $2/\alpha(\partial \alpha/\partial p)_\tau$. Our present theory leads us to replace this by the statement that there is a lower limit one half the value previously found. Now it is true that twice the amplitude represented a somewhat better approximation to the average of all the results than did the expression of Grüneisen, for example, which was the best of other theoretical expressions for the pressure coefficient of resistance, but there were deviations from it in both directions. It is on the other hand true that there are no cases known, either among the substances of the previous work or among the new elements of my more recent work, except those abnormal metals for which the coefficient is positive, and which will be dealt with separately later, in which the coefficient falls as low as $1/\alpha(\partial \alpha/\partial p)_\tau$. So that although our present theory is not complete because of the unknown element of atomic struc-

ture, it is at least more satisfactory than the former attempt in that it is true without exception.

So much for the formal expression of the theory with regard to temperature and pressure changes of resistance. The classical expression for thermal conductivity is to be taken over without change, and need not be written down explicitly. It gives the right order of magnitude for the Wiedemann-Franz ratio, but is not a complete expression of the facts because it neglects the part of conduction done by the atoms, and hence will be expected to fail particularly at low temperatures, where the atomic conduction becomes important.

The theory as outlined is not inconsistent with a retention of the classical expression for the Peltier heat. In particular the theory is in accord with the classical theory in at least two aspects of thermoelectric phenomena. The magnitude of the pressure coefficient of the thermo-electric force would mean, according to the classical theory, that the number of free electrons does not change much with increasing pressure. This is in exact accord with the assumptions of our theory. Furthermore, the small Peltier heat between a solid and a liquid metal makes it likely that the number of free electrons is not greatly different in solid and liquid. As will be seen in the following, our theory gives an account of the difference of resistance between solid and liquid in terms of a difference of free path only, without supposing a difference in the number of electrons. There was here a weak point of the classical theory, because to account for the great difference of conductivity between solid and liquid it had to suppose a number of electrons much greater in the solid than in the liquid, which was not consistent with the thermo-electric phenomena. At the same time I do not believe that it is desirable to take over entirely the whole classical picture of the mechanism of thermo-electric action. There are, of course ions as well as wandering electrons present in the metal, and these ions may play a part in thermo-electric action, although because of their relatively small translational velocity their part in conduction may be altogether insignificant. That some such modification is necessary is indicated by the fact that the classical expression for the Thomson heat demands that the number of free electrons increase as the square root of the absolute temperature, whereas we have assumed that the number is constant. However, the Thomson heat is relatively a small matter, and I have not attempted to bring it within the range of the present theory. If the above considerations are sound it ought to be possible to get it in without essentially modifying the mechanism which we have set up to account for conductivity.

This is as far as I have got at present with the quantitative develop

ment of the theory. Its advantages are obvious. It gives an unforced and inevitable description of the variation of resistance with temperature, predicts the right sign and an important part of the numerical magnitude of the pressure coefficient, avoids the difficulty of the classical theory with the specific heats while retaining the classical explanation of the Wiedemann-Franz ratio, and leaves open the possibility of much greater conductivity or even superconductivity at low temperatures, which was not possible to the classical theory. Further development of this theory seems to demand more intimate knowledge of atomic structure than we have at present.

But in addition to these quantitative facts, the theory is able to bring a very large number of facts qualitatively into line, as was emphasized in the preceding paper. In the following I give a survey of the new facts brought out by the new experimental work, and the relation of the theory to these facts.

1. The view of conduction as due to the passage of electrons from atom to atom through the substance of the atom receives confirmation from a group of phenomena not considered in detail in the previous paper, namely the phenomena of the resistance of alloys. Alloys fall into two main groups, according as they do or do not form mixed crystals. Those alloys which do not form mixed crystals solidify by the separation of the two components each in a pure condition, so that the solid alloy consists of a mechanical mixture of microscopic crystals of the two components. It would be expected that the resistance of a mixture of this sort would be the mean of the resistance of its components, and it is indeed the experimental fact that the resistance of such alloys can be computed by the rule of mixtures. The other class of alloys is one in which mixed crystals are formed, the atoms of the two metals entering side by side into the same crystal edifice. This is possible because of a certain degree of resemblance of the two kinds of atoms. The resemblance is not complete, however, and the indiscriminate use of either kind of atom in the crystal edifice is possible only with a certain amount of distortion in the final result. It is a fact that most mixed crystals will not accept an unlimited amount of the foreign ingredient, but the two atoms will crystallize side by side only up to certain limiting proportions. In the mixed crystal structure we would expect, therefore, a certain amount of imperfect fitting between adjacent atoms, with the result that the electrons encounter difficulty in passing from atom to atom, so that, because of the extra resistance of the "gaps" between the atoms, the resistance of the alloy is greater than that computed from the components. This is in exact accord with the experimental facts.

Furthermore, the temperature coefficient of alloys is strikingly accord with this view. The temperature coefficient of those alloys whi do not form mixed crystals is the same as that of the pure metals, whi is what we would expect, but the temperature coefficient of those allo in which there are mixed crystals is very much less than that normal to pure metal. A large number of binary alloys satisfy Matthiesen's ru in this regard. If we write the resistance of the alloy in the form

$$R_A = R_M + \Delta R,$$

where R_A is the resistance of the alloy, R_M the resistance which woul be computed according to the rule of mixtures, and ΔR the resistanc which must be added to the computed resistance to give the actua resistance, then Matthiesen's rule states that the temperature coefficien of the alloy is given by the expression

$$\frac{dR_A}{dt} = \frac{dR_M}{dt}.$$

This means that $d\Delta R/dt = 0$, or the additional resistance is not affected by changes of temperature. This is in precise accord with our point of view, for the additional resistance (ΔR) is due to the lack of perfect fit between adjacent atoms of different kinds, and this would be expected to be relatively little affected by changes of temperature.

It is also an experimental fact that the resistance of alloys tends to a finite value at 0° Abs., instead of vanishing like that of a pure metal. This merely means that the gaps between the different kinds of atoms persist to low temperatures, as we would certainly expect.

2. The fact that the resistance of a metal increases on hard drawing is consistent with this point of view. During hard drawing the crystal grains are broken up, and the fitting of the atoms is rendered less exact on the average. This is proved by the universal fact that during hard drawing the density of the metal decreases. But such a disarrangement of the fitting of the atoms means an increased chance of interference when the electrons pass from atom to atom, and consequently an increase of resistance.

Tammann[1] has given an explanation of this fact on the basis of a difference of resistance in different directions within the crystal grains. It would seem, however, that this explanation must be rejected, because the resistance of a cubic crystal is independent of direction (see Voigt, Krystal Physik, pp. 311, 313), whereas the phenomena of increase of resistance on hard drawing is shown by all metals, regardless of their crystal system.

[1] G. Tammann, Lehrbuch der Metallographie, Leopold Voss, 1914, 117–120.

3. It has been observed that as the proportions of the components change through a series of alloys forming mixed crystals the electrical resistance increases in that direction in which the mechanical hardness also increases. Now an increased mechanical hardness means an increased staggering in the positions of the atoms in the crystalline grains, so that it is more difficult to produce sliding of one part of the crystal on another, and by the same token an increase in the difficulty of the electrons in making the leap from atom to atom.

4. In the previous paper a suggestion was made as to the possible explanation of the positive pressure coefficient of bismuth and antomony. The idea was that the amplitude might increase with increasing pressure instead of decreasing as normal. It was shown in that paper that the fact that both metals expand on freezing indicates that there is a certain relative position of the atoms in which the repulsive forces are unusually large at an unusual distance of separation, and that the atoms crystallize in this relative position. From a grossly material point of view this may be expressed by saying that the atoms have knobs, and that the metal crystallizes with the knobs in contact. On the average, except for these knobs, the bismuth atom may be much like that of other metals. The fact that the repulsive forces are unusually large at an unusual distance of separation of the atomic centers is compensated for by an unusually slow decrease of the repulsive force as the distance between atomic centers is decreased. This slow change of the repulsive force was shown in the preceding paper to be consistent with a decreasing frequency of atomic vibration as the centers are brought closer together, and hence consistent with an increasing amplitude with increasing pressure.

This view receives interesting numerical confirmation from recent work of Grüneisen[1] on the equation of state of solids. He has shown that it is possible to a good degree of approximation to explain the behavior of solids by supposing that at least over a small range the forces between atoms are represented to a sufficient approximation by the expression

$$f = \frac{A}{r^2} + \frac{B}{r^m},$$

where the first represents a force of attraction, and the second a force of repulsion. In general m will be much larger than 2. Its magnitude will give an idea of how rapidly the repulsive force increases as the atoms approach. Grüneisen gives an equation for m in terms of atomic volume, atomic heat, thermal expansion, and compressibility. It is not necessary

[1] E. Grüneisen, Ann. Phys., 39, 257–306, 1912.

to reproduce the expression here. Grüneisen finds that m varies for normal metals from 7.5 for iron to 15.6 for gold. If we apply Grüneisen's formula to bismuth and antimony we find that m for the latter is 3.8, and for the former 4.5, both very much less than for normal metals. Our point of view is confirmed, therefore, that the repulsive forces in bismuth and antimony increase more slowly than normal as the distance between atomic centers is decreased, and therefore we have the possibility of an increasing amplitude with increasing pressure and so an increasing resistance.

5. The fact that the temperature coefficients of solid bismuth and antimony are normal is quite in accord with our view, for with rising temperature we have seen that the effect of temperature on increasing amplitude quite overshadows any pure volume effect, so that we would expect the temperature coefficients of all metals to be nearly the same, irrespective of the behavior of the pressure coefficient.

6. The fact that the pressure coefficient of liquid bismuth is normal in being negative is significant. It indicates that the positive coefficient of the solid is in some way connected with the crystalline structure. The picture which we have given of the mechanism of the positive coefficient of the solid has this property, for we have ascribed the increasing amplitude with increasing pressure in the solid to the fact that the atoms are held in fixed orientations with respect to each other, and that in this particular orientation the forces are abnormal in character. Such a fixity of orientation is possible only in the crystal. In the liquid there is no definite relation of orientation, the localities of abnormal force play a relatively unimportant part, and the liquid behaves normally. Not only is the pressure coefficient of liquid bismuth normal, but the temperature coefficient is also normal for a liquid, and is less than that of the solid, and less than the reciprocal of the absolute temperature.

7. It was shown in the previous paper that the abnormality of force between the atoms of bismuth made possible a crystal with abnormally large volume, and hence a crystal which expands on freezing. By analogy I was prepared for a positive pressure coefficient in gallium, which is also abnormal in expanding on freezing. The facts are the opposite, however, and the pressure coefficient of gallium is negative, as is normal. Our previous argument was entirely qualitative, however, and merely indicated the tendency toward an increasing amplitude with increasing pressure without setting up a criterion as to whether the tendency might be strong enough to counteract the normal tendency in the opposite direction or not. In the absence of a definite criterion therefore, we have only the right to expect the same tendency in gallium without

actually being sure whether the tendency will be strong enough to make the coefficient positive. Now as a matter of fact, if the expected magnitude of the pressure coefficient is calculated by the method of the previous paper, it will be found that the discrepancy for gallium is greater than for any other substance with negative coefficient, the calculated value being about twice the observed value. This means that the pressure coefficient is much less than we would expect from the behavior of normal substances, so that here we evidently have the tendency which we are looking for toward a positive coefficient.

In other respects the behavior of gallium is as we would expect. The temperature coefficient of the solid is normal, and the temperature coefficient of the liquid is also normal in being less than that of the solid. Furthermore, the pressure coefficient of the liquid is normal, and is greater numerically than that of the solid, as we would expect, because the tendency to abnormality in the solid is due to a particular orientation of the atoms, and this disappears in the liquid.

8. The behavior of lithium is of a type not shown by any other substance yet known. Its pressure coefficient is positive in both solid and liquid, and the coefficient of the liquid is greater than that of the solid. The temperature coefficient behaves normally. Furthermore, the melting of lithium is normal, in that the liquid has a larger volume than the solid. The data seem not to have been previously determined. In the paper on new resistance data will be found the melting data for lithium which I determined for this particular purpose. I have followed the melting curve up to 8,000 kg., and it seems normal in every respect. Our picture of the mechanism of conduction in lithium must probably, therefore, be different from that of bismuth or antimony or gallium. It is of course possible that the explanation of the abnormal coefficient follows on the same lines as for other metals, namely an increasing amplitude of atomic vibration with increasing pressure. If this explanation is adopted, the abnormality of the atom must not be thought of as confined to certain localities which function only in the crystalline phase, but the abnormality must be one of the atom as a whole, for the liquid as well as the solid is abnormal. This is not an impossible view, for if m be calculated for lithium by Grüneisen's formula, the value 5 will be found, which is low compared with most other metals, but is not low compared with bismuth and antimony. But now the question arises as to the interpretation to be put on the value of m. m itself merely is a measure of the rapidity with which the repulsive force increases as the atom is approached. A low value may be due either to an abnormality of a particular part of the atom, as we have supposed the case with bismuth

and antimony, or it may indicate that the atoms are separated by more than the usual distance, and the repulsive force is not important. We would expect the latter view to be more nearly correct for substances which are very compressible. This seems indicated by the fact that m is as small for the very compressible elements sodium and potassium as it is for lithium, and sodium and potassium have very large negative pressure coefficients of resistance. Now lithium is also one of the most compressible metals. It seems likely to me that the low value of m is more probably connected in some way with the high compressibility than with an abnormality which might result in an increasing amplitude of atomic vibration with increasing pressure.

Now there is a picture of conduction offered by the theories of Wien[3] and Lindemann[1] which gives an alternative explanation, which may quite probably be correct for this particular substance. Their picture is of electrons as well as atoms located on a space framework, and of the space framework of electrons moving bodily through the framework of the atoms when an external force is applied. The mean free path of the electrons in this motion is interrupted by collisions with the nuclei of the atoms. This picture means a positive pressure coefficient of resistance for most substances, for as pressure is increased the channels of passage of the electrons become more restricted. The reason for this is that the closing in of the channels because of the decreasing distance between atomic centers more than neutralizes the opening of the channels because of decreasing amplitude of atomic vibration. This is in spite of the fact that the relative change in atomic amplitude is much greater than the relative change in the distance between atomic centers, because the distance between atomic centers is absolutely much greater than the amplitude. It will be found as a matter of fact that if the relative magnitudes of atomic distance and amplitude and of the changes of atomic amplitude and distance with pressure be calculated for lithium, Wien and Lindemann's picture would lead us to expect a positive pressure coefficient. Evidently the positive pressure coefficient suggested by this picture remains true for the liquid state so long as the electrons continue to move between the atoms.

Apart from the argument from the pressure coefficient, this picture of Wien and Lindemann seems to have a particular probability of being correct for lithium because of its atomic structure. The structure is a simple nucleus consisting of a central positive charge and two electrons rotating about it, and a single other electron connected in some way with the nucleus at a relatively large distance. If the superficial electrons of

[1] F. A. Lindemann, Phil. Mag., 29, 127–140, 1915.

the atom are ever to arrange themselves into a space lattice, it would seem that here is their chance.

The fact that the pressure coefficient of liquid lithium is larger than that of the solid is simply explained as due to the greater compressibility of the liquid. The compressibility of the liquid has never been measured, but there is no case known in which the liquid does have a smaller compressibility than the solid, and furthermore the behavior of the melting curve, its direction of curvature, and the direction of the difference of volume between solid and liquid, makes it almost inevitable that the compressibility of the liquid be greater than that of the solid.

The fact that the pressure coefficient of resistance becomes greater at higher pressures is also intelligible from this point of view. The channels through which the electrons slip are the spaces which are left between atomic centers after the inpenetrable nucleus has been subtracted. Hence a given proportional decrease in the distance between atomic centers will mean a greater proportional decrease in the channel when the atoms are close together (high pressures) than when they are further apart.

9. On the other hand, the increase of the pressure coefficient of bismuth and antimony with increasing pressure is at least perfectly consistent with the picture presented of their conduction as performed by electrons passing through the atoms instead of between them. If reference is made to Fig. 1 of the previous theoretical paper it will be seen that it is quite possible that as the atomic centers approach the restoring force per unit displacement becomes weaker. In fact such a behavior is inevitable at some value of the volume, but we have no criterion for deciding whether this takes place at a volume greater or less than the volume at which the crystal is stable. Now such a weakening of the restoring force when the volume decreases means an amplitude of vibration becoming progressively larger at the higher pressures (smaller volumes), and hence a pressure coefficient increasing with increasing pressure.

10. The pressure coefficients of calcium and strontium were also found to be positive. It is difficult to decide from the data at hand whether this is more probably due to the lithium or the bismuth type of mechanism. The melting data are not known for either of these metals, so that we do not know whether the liquid or the solid has the greater volume. Neither are the data known for the effect of pressure on the resistance of the liquid. It is true that the value of the "m" of the atomic force calculated for calcium is somewhat lower than for the ordinary run of metals, being 6, but the compressibility of calcium is also high, and the m

for strontium is distinctly high, being 0.5. It is, of course, probable that the mechanisms of calcium and strontium are the same, because of their similar positions in the periodic table. I believe that at present the probability is in favor of the lithium rather than the bismuth type of conduction. The melting data would be a great help toward this decision.

11. There is an interesting relation between the temperature coefficients of solid and liquid lithium. At the melting point of lithium, 180°, the temperature coefficient of the solid is 0.00251 (obtained by a linear extrapolation of the resistances at 0° and 100° and therefore somewhat uncertain, but the best that we can do), and the coefficient of the liquid is 0.00150. The ratio of these two coefficients is 1.69, which is almost exactly the ratio of the specific resistance of the liquid to that of the solid at the melting temperature, for which I found the value 1.68.

This can be easily understood in the light of Wien and Lindemann's picture. The resistance of the liquid is higher than that of the solid because the regular channels between the atoms are broken up by the haphazard arrangement of the atoms in the liquid. Now this factor of random arrangement of the atoms in the liquid is one that will persist at all temperatures, producing a permanent difference of resistance between solid and liquid. This can be given mathematical expression. Write the equation

$$R_L = R_S + \Delta R,$$

where R_L is the resistance of the liquid, R_S the resistance of the solid, and ΔR the increment of resistance on passing from solid to liquid. Now differentiate with respect to the temperature

$$\frac{1}{R_L}\frac{dR_L}{dt} = \frac{R_S}{R_L}\cdot\frac{1}{R_S}\frac{dR_S}{dt} + \frac{\Delta R}{R_L}\cdot\frac{1}{\Delta R}\frac{d\Delta R}{dt}.$$

If the experimental relation

$$\frac{1}{R_L}\frac{dR_L}{dt} = \frac{R_S}{R_L}\cdot\frac{1}{R_S}\frac{dR_S}{dt}$$

is to hold, then we must have $d\Delta R/dt = 0$. That is, the increment of resistance when the solid passes to the liquid is independent of temperature, which is what our picture suggested.

12. The same relation between the temperature coefficient of the solid and the liquid holds for some other metals. Thus for sodium at the melting point at atmospheric pressure I found for the coefficient of the solid 0.00414, and for the liquid 0.00310. The ratio of these is 1.34, and I found experimentally the ratio of the resistance of the liquid to that of the solid to be 1.45. Mercury has the largest ratio observed for the

ratio of specific resistance of liquid to solid, and we would therefore expect an unusually small temperature coefficient for the liquid. It is in fact unusually small, being only 0.00090 at 0° C. If we assume that the coefficent of the solid is $1/\tau$, we find for its coefficient at the melting point (− 38.85°) 0.00409, and for that of the liquid at the same temperature 0.000934. The ratio of these is 4.38 and the ratio of the resistance of the liquid to the solid found by Onnes[1] is 4.22. On the other hand, the relation breaks down for solid and liquid potassium. I find that the temperature coefficient of the liquid is actually slightly greater than that of the solid at the melting point, which is abnormal, whereas the resistance of the liquid is 1.56 times greater than that of the solid. It might be mentioned that my figures for the temperature coefficients of solid and liquid do not agree with those of other observers. The values of Northrup[1] are most favorable to the hypothesis being urged here. He makes the coefficient of liquid potassium less than that of the solid, but the ratio of the two coefficients as found by him is only 1.27, whereas the ratio of specific resistances would demand 1.56.

The only other metals for which I have determined the coefficients, namely bismuth and gallium, cannot possibly satisfy the relation because the temperature coefficients of the solid are greater than those of the liquid, as is normal, but the resistance of the liquid is less than that of the solid. This is because of the abnormal volume relation, so that we are not surprised that the relation breaks down.

There are also some data of Northrup[3] for other metals. For gold his data give a ratio of the temperature coefficients at the melting point of 2.15, and he found for the ratio of the resistances 2.28.

Now with regard to the explanation of this relation between the temperature coefficients, our point of view would lead us to expect an invariable element, unaffected by changes of temperature, in the relative resistances of solid and liquid, and hence, according to the analysis, a ratio of the coefficients equal to the inverse ratio of the resistances. When the solid melts to the liquid the atoms lose their regular mutual arrangement, which becomes haphazard. In passing from atom to atom in the liquid the electrons cannot avail themselves of particularly favorable localities, but must use the average of the entire atom. This element will be a permanent difference between solid and liquid, unaffected by changes of temperature. However, the relations are so complicated that this can be only part of the picture, and in fact the relation

[1] K. Onnes, Kon. Akad. Wet. Proc., 4, 113–115, 1911.

[2] E. F. Northrup, Trans. Amer. Elec. Chem. Soc., 20, 185–204, 1911.

does not always hold. There is a specific effect due to the "τ" term in our formula for resistance. This may to some extent be neutralized by the tendency of the "gaps" in the liquid condition to function in the second way, decreasing instead of increasing the resistance with increasing amplitude. Furthermore, it is not certain to what extent our deduction of the variation of amplitude with temperature and pressure is valid for the liquid. We assumed that the energy of atomic vibration was either potential or else kinetic energy of to and fro motion. Now in the liquid there is probably some rotational energy as well. The exact relation between the translational and the rotational energies in the liquid is not yet clear, so that we do not know how large an effect to expect on this account. It seems evident, however, that the direction of the effect will be to decrease somewhat the temperature coefficient of amplitude, because part at least of the energy will be rotational, and therefore the translational energy, and so the amplitude, cannot increase as rapidly with increasing temperature as if we had supposed all the energy to be translational.

The entire theoretical significance of this observation as to the ratio of the temperature coefficients of solid and liquid may therefore not yet be completely clear, but at any rate the observation itself is to be kept in mind. I am not aware that this relation has been previously noticed.

13. The considerations of the last section have an application to the temperature coefficient of resistance of the liquid at high temperatures. Write the formula for the resistance in the form

$$R_L = \text{const } \tau^{1/2}/l_L.$$

Now the free path, l_L, is inversely proportional to the chance, β, that the free flight of the electron will be terminated in passing from atom to atom. Let us analyze this chance of termination into two parts. One will depend on the haphazard orientation of the atoms with respect to each other, and will be independent of temperature, and the other will depend on the amplitude, and will, as before, be proportional to the amplitude, if we can neglect the pure volume effect, and the tendency of the gaps to function in the second way. Hence we may write

$$\beta = A_1 + A_2\alpha,$$

which gives

$$R_L = \text{const } \tau^{1/2}(A + \alpha).$$

Differentiate this with respect to the temperature, giving,

$$\frac{1}{R_L}\frac{dR_L}{d\tau} = \frac{1}{2t} + \frac{\alpha}{A + \alpha}\cdot\frac{1}{2\tau}.$$

Hence we see that at high temperatures, where α is large, the temperature coefficient again approaches $1/\tau$, although at lower temperatures it is less than $1/\tau$. These considerations apply only to those liquids for which the functioning of the gaps by decreasing resistance at large distances of separation may be neglected. Now there are liquids for which this last factor is certainly important, as zinc and cadmium, whose temperature coefficients immediately after melting are negative, but there are other liquids, as tin and lead, whose resistance in the liquid shows no peculiarity. The resistance of these liquids increases linearly with the temperature. In fact the linear increase of the resistance of tin is so striking that Northrup and Suydam[1] have proposed this as the basis of a resistance thermometer. Now it is evident that the temperature coefficient of any metal which increases linearly in resistance with temperature must eventually become equal to $1/\tau$, according to the above formula.

14. The very large difference of resistance between solid and liquid mercury is striking, particularly in view of the fact that the change of volume on melting is not larger than usual. This would suggest that the structure of the mercury atom is such that the element of haphazard orientation is particularly important. This element we saw has a tendency to constancy. Consider now the variation of resistance with pressure. I found experimentally that the pressure coefficient of the liquid is less numerically than that of the solid, a somewhat unexpected result. Write

$$R_L = R_S + \Delta R.$$

Differentiate with respect to the pressure

$$\frac{1}{R_L}\left(\frac{\partial R_L}{\partial p}\right)_\tau = \frac{R_S}{R_L}\cdot\frac{1}{R_S}\left(\frac{\partial R_S}{\partial p}\right)_\tau + \frac{\Delta R}{R_L}\cdot\frac{1}{\Delta R}\left(\frac{\partial \Delta R}{\partial p}\right)_\tau.$$

This equation shows at once that the experimental relation

$$\frac{1}{R_L}\left(\frac{\partial R_L}{\partial p}\right)_\tau < \frac{1}{R_S}\left(\frac{\partial R_S}{\partial p}\right)_\tau$$

demands that

$$\frac{1}{\Delta R}\left(\frac{\partial \Delta R}{\partial p}\right)_\tau < \frac{1}{R_S}\left(\frac{\partial R_S}{\partial p}\right)_\tau,$$

which is what our picture led us to expect. Notice that we have disregarded the pure volume effect, so that these considerations would not be expected to apply to a highly compressible metal. Mercury, however, is relatively incompressible, and the considerations have a certain force.

15. A similar consideration applies to the pressure coefficient of alloys. The pressure coefficient of resistance of the alloys of the relatively in-

[1] E. F. Northrup and V. A. Suydam, Jour. Fran. Inst., 175, 153–161, 1913.

compressible metals is usually less than that of the components. This is to be ascribed to a relative insensitiveness to pressure of the feature which is responsible for the increased resistance of the alloy. This feature is the failure of the exact register of the different kinds of atoms, and this feature will be insensitive to pressure unless the atoms themselves are highly deformable. The data for alloys are very restricted, and it is not known how the alloys of such very compressible metals as sodium and potassium would behave under pressure.

16. The same considerations also show why the ratio of resistance of solid to liquid is relatively constant along the melting curve. For the six substances which I measured this ratio suffered relatively little change, although the accuracy of the measurement was not as great as desirable in some cases. This constancy is to be ascribed to the fact that the effect of haphazard orientation in the liquid as opposed to the regular arrangement in the crystal is an intrinsic difference between solid and liquid, and is not affected by temperature and pressure changes.

17. In my previous paper some significance was attached to the fact that the temperature coefficient of liquid mercury at constant volume is negative. This was ascribed to the second manner of functioning of the gaps at the increased volume of the liquid. It was suggested that such might be found to be the case for all liquid metals. At the same time there was no necessity in the suggestion, and there was no criterion which could show whether the second manner of functioning of the gaps would be more important than the normal method for other metals or not. It appears that this is not the case for the new metals. The computation could be made only for sodium, potassium, and bismuth. The values of the thermal expansion are not known for liquid gallium. For lithium, because of the abnormal pressure coefficient of the liquid, the temperature coefficient of the liquid at constant volume is even larger than at constant pressure, and is of course positive. The computation for the three metals above is somewhat uncertain because the compressibility and thermal expansion of the liquids are not known with any great accuracy. A discussion will be found in the new American Academy paper. I find for sodium that the coefficient at constant pressure is 0.00325 against 0.00170 at constant volume; for potassium the respective coefficients are 0.0044 and 0.0025, and for bismuth they are 0.000475 and 0.000015. The uncertainty in the fundamental data is not so great but that there can be no doubt that the coefficients at constant volume of both liquid sodium and potassium are positive, but there may be considerable question in the case of bismuth.

Sodium and potassium are among the most compressible and ex-

pansible of the elements, and it is perhaps not surprising that for them the amplitude continues to function in the normal manner. The example of bismuth makes it not unlikely, however, that the coefficient at constant volume of the ordinary liquid metals may be negative, as it is for mercury, instead of positive. It is in any event significant that the difference between the coefficients at constant volume and constant pressure of all the liquid metals is greater than the difference for the solid, so that the tendency of the gap to function in the second way is manifest.

The second manner of functioning of the gap in liquid mercury may at first seem inconsistent with the relative constancy of the gap under pressure, which we invoked to explain the pressure coefficient of the liquid being less than that of the solid. But it is to be remembered that a change of temperature is always more effective than a change of pressure (compare the magnitudes of the compressibility and the dilatation) so that the two facts are not inconsistent. It is also to be kept in mind that the difference of compressibility between solid and liquid mercury is abnormally small.

18. The behavior of the alkali metals sodium and potassium is of interest because of the unusual magnitude of the effect, and demands special discussion.

In the first place I may mention in the interest of candidness that I had anticipated a possible positive pressure coefficient for potassium on the basis of the similarity of the structure of its atom to that of lithium. According to Langmuir's picture,[1] lithium consists of a positive kernel surrounded by one shell, with a single electron outside that shell, whereas potassium consists of a positive kernel, two surrounding shells, and a single electron outside the two shells. This similarity would seem to give some justification for the expectation of a positive pressure effect. However, the facts are the exact reverse. Not only is the pressure coefficient of potassium negative, as is normal, but it is larger than for any other metal as yet measured. It would seem, therefore, that the greater size of the central portion of the atomic structure of the atom of potassium prevents the arrangement of the superficial electrons in a space lattice, or at least is not favorable to the ready mobility of such a lattice, if it exists. The mechanism of conduction in the case of potassium is probably normal, in that the electrons pass through the substance of the atoms. It must be said, however, that potassium is abnormal in several respects. My measurements make the temperature coefficient of the liquid at the freezing point greater than that of the solid, and the pressure

[1] I. Langmuir, Jour. Amer. Chem. Soc., 41, 868–934, 1919.

effects are abnormal in that the coefficient of the liquid decreases with increasing temperature. It is therefore not impossible that part of the mechanism of conduction of potassium is abnormal.

If the expected magnitude of the pressure coefficients of sodium and potassium is computed on the basis of the preceding paper from twice the pressure coefficient of amplitude, it will be found in both cases that the computed values are very much too small. The observed coefficient of sodium is 1.75 times the computed, and the observed value for potassium is 2.4 times that computed. According to our view, this means an unusually large volume effect in addition to the amplitude effect. Now not only are the compressibilities of sodium and potassium among the highest of the elements, but the change of atomic distance with pressure is an unusually large fraction of the change of amplitude, so that for this additional reason we would expect a large volume effect. If the ratio of the pressure coefficient of amplitude to the coefficient of linear compressibility be computed, by the use of formulas already given, the values 3.8 and 3.6 will be found for sodium and potassium respectively. This is unusually small, we have already seen that the run of values for the ordinary metals is from 6 to 9. Lithium is the only metal which is markedly lower, and for this the ratio is 0.95, but since its conduction mechanism is abnormal, we need not consider it further. It is, then, just for such metals as sodium and potassium that our picture would lead us to expect the largest discrepancy between the amplitude and the total effects, and it is just here that we find them.

Sodium and potassium are also unusual in the large decrease of the pressure coefficient with increasing pressure. Between atmospheric pressure and 12,000 kg. the instantaneous coefficient of sodium has decreased by a factor of 2.5, and that of potassium by 2.6. In the previous work the largest decrease was for lead, with a factor 1.38. The large decreases for sodium and potassium are evidently connected with the unusually high compressibilities. It is a universal result of experiment that those substances with a high compressibility show not only an unusually large absolute decrease of compressibility with rising pressure, but the relative decrease is also unusually high. The actual data have not been determined for sodium and potassium, but we have every reason to expect that the same will be found to hold for them also. This means that the volume effect becomes relatively less at high pressures, and that the pressure coefficient decreases by an unusually large amount.

In addition to the unusually large decrease of pressure coefficient with increasing pressure, there is an unusually large change of the coefficients with temperature. The pressure coefficient increases with rising tempera-

ture by an unusually large amount, whereas the metals of the previous paper showed relatively little change with temperature. The coefficients of sodium at atmospheric pressure increase by a factor of 1.18 between 0° and 80°. The corresponding comparison cannot be made for potassium, because it is not solid over a wide enough range, but a comparison of the results at higher pressures shows that the change for potassium is even more rapid than for sodium. Of course a mathematical consquence of a pressure coefficient changing rapidly with temperature is a temperature coefficient changing rapidly with pressure. This effect again can be explained on the basis of the volume effect. Sodium is unusually expansible at atmospheric pressure, and we would expect a temperature coefficient considerably greater than that computed on the basis of the amplitude effect alone, that is, a coefficient greater than $1/\tau$. And as a matter of fact, the average coefficient of sodium between 0° and 100° is 0.00475, larger than $1/\tau$ by an unusual amount. Now at higher pressures, although the actual measurements have not yet been made, it is exceedingly probable that the volume expansion will show an unusually large decrease, and that sodium will approach more nearly the behavior of the more staid metals. The behavior of the temperature coefficient is in entire accord with this expectation, at 12,000 kg. it has dropped from 0.00475 to 0.00408, a value still somewhat larger than $1/\tau$, but not any larger than for many of the other metals at atmospheric pressure.

These considerations would lead us to expect the temperature coefficient to become not less than $1/\tau$ for any pressure, no matter how high, as long as the atomic vibration continues to function in the normal way in decreasing the probability of an undisturbed flight of the electron. It is conceivable that at exceedingly high pressures the atom itself may become so much compressed that a moderate amount of temperature disturbance is not sufficient to interfere at all with the chance of passage of an electron from atom to atom. The kinetic energy of temperature agitation in such a solid would consist in a quivering of the nucleus within the outer structure of the atom, which is prevented from much superficial motion by the close packing of the adjacent atoms. This state of affairs demands an unusually small thermal expansion. If such a state of affairs should occur, we might expect the temperature coefficient of resistance to become less than $1/\tau$. Now this is actually what does occur with potassium. Its mean temperature coefficient between 25° and 60° decreases from 0.00454 at atmospheric pressure to 0.00184 at 12,000 kg., the final value thus being much less than $1/\tau$. This speculation is most attractive, but more weight cannot be attached to it until

the dilation of potassium has been measured at high pressures. It may be said that if this effect is to exist anywhere, it has the best chance with potassium of the metals measured, since it is by far the most compressible. Potassium is a trifle more than twice as compressible as the nearest metal sodium. And in further support of this view it may be noticed that the temperature coefficient of potassium at 6,000 kg. has dropped only to 0.0034, and it is therefore still a little higher than $1/\tau$ ($\tau = 298°$ Abs.), so that the decrease of the temperature coefficient becomes increasingly rapid at higher pressures, a most unusual behavior for a pressure effect. In caution it may be said that the experimental accuracy in determining the variation of the coefficients of potassium was not so high as for some other substances. It will be most interesting to attempt the verification of this observation on cæsium, which is almost twice as compressible as potassium.

If this observation should be justified by the measurements of thermal expansion, it would be a further most important verification of the view that the free flight of the electrons is interferred with during the passage from one atom to another, and that the interference is not due to the vibration of the nucleus, for the temperature agitation of the nucleus must continue to exceedingly high pressures.

19. The new data cover the non-metallic elements carbon and phosphorus (black). It is probably too early to extend this theory to all non-metallic substances, but it is interesting that in two important particulars the behavior of carbon and black phosphorus is what we would expect. We have thought of the gaps between atoms as functioning in two ways. Normally in metals the electrons leap easily across the gaps, and their passage is made more difficult by temperature agitation. The gaps, when in this condition, have a low specific resistance. But when the atoms are separated by more than the usual amount the electrons usually find difficulty in leaping the gaps, which are thus of high specific resistance, but the passage may be made more easy by increasing violence of temperature agitation, which brings the atoms closer together during part of their vibration. If the gaps are on the average in this second condition, we expect a high specific resistance for the substance as a whole, and a negative temperature coefficient of resistance (at least at constant volume, and presumably at constant pressure). Now these are the facts for both carbon and black phosphorus. Their specific resistance is much higher than that of any metal, but their temperature coefficient is negative.

It is also natural to expect that in such a substance the effect of pressure will be to drive the gaps from the second condition to the first as the

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atoms are brought closer together. This means an unusually large decrease of resistance with pressure. This is the fact for black phosphorus. The pressure effect is larger than for any other substance, and is so large that at 12,000 kg. the resistance is only 3 per cent. of its value at atmospheric pressure. Even after this enormous decrease the resistance is still much higher than for metals. The specific resistance of black phosphorus normally is 1 ohm per cm. cube, and therefore at 12,000 kg. it is still 0.03. The temperature coefficient at 12,000 kg. is still negative, but has dropped numerically from 0.0058 to 0.0030, which is in the direction to be expected as the resistance approaches that of a metal in character. The pressure effect on black phosphorus is different in another respect from that of metals, in that the relative coefficient $1/R(\partial R/\partial p)_\tau$ is very nearly independent of pressure. We saw that for metals this coefficient decreases with increasing pressure, and we gave as the explanation the decreasing compressibility with increasing pressure. It is evident that the mechanism is different in the case of black phosphorus. A constant coefficient would mean that a constant increment of external pressure always drives the same fraction of the total number of gaps from the second into the first group. We would expect this condition to hold as long as the number of electrons in the second group is still large. That this number still is large, even under 12,000 kg., is shown by the fact that under 12,000 kg. the resistance is still very much higher than for metals.

CONCLUSION.

We have now considered a great many of the phenomena of the electrical resistance of metals, and found them all consistent with the view of the nature of electrical conduction previously advanced. The facts considered in this paper were nearly all not known when the view was first suggested and are different in character from any previously available, having largely to do with the pressure and temperature changes of resistance of both the liquid and the solid metal, particularly of the alkali metals, in which the effects are very large.

The view of conduction is that the free paths of the electrons are interfered with in jumping from atom to atom, but that throughout the interior of the atom there is no resistance to their motion. We have put this conception into quantitative form, partly on the basis of the classical theory. At ordinary temperatures we have assumed the equipartition velocity of the electrons, that their number is independent of the temperature, and that the free path varies with the amplitude in a way which may be computed. This gives Ohm's law, the correct temperature coefficient, the Wiedemann-Franz ratio, an important part of the pressure

effect, vanishing resistance at 0° Abs., and avoids the specific heat difficulty. In addition there are certain features which can be discussed only qualitatively; there is a specific effect of changing volume of which we may be pretty sure of the sign, but which depends in an unknown way on atomic structure, and there is a second manner of functioning of the "gap" at large volumes. Within the restricted range open to quantitative discussion the facts are in accord with the theory, and throughout the much wider domain open to qualitative discussion I have not found a single fact which is inconsistent, and many which I believe demand this view uniquely.

The probability seems great that the view contains the most important elements operative in the phenomena of resistance and thermal conduction in metals. This theory does not exclude the presence of other factors which may be important for the thermo-electric and the Hall effects. In fact our theory has made it inevitable that there should be in the metal charged ions as well as the electrons, and there is no reason why these should not be important in certain phenomena, although because of their low velocity of translation they cannot be expected to play a large part in conduction.

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ELECTRICAL RESISTANCE UNDER PRESSURE, INCLUDING CERTAIN LIQUID METALS.

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Introduction.

In an earlier investigation [1] I have determined the effect of pressure on the resistance of a number of the metallic elements, and have considered the significance of the results for theories of metallic con-

duction. The results then obtained suggested a number of important questions which could not then be answered because the data had not been determined. In particular, the effect of pressure on the resistance of only one liquid metal had been measured, mercury, and the comparative effect of pressure on the resistance of the same metal in the solid and the liquid state was not known for any substance. Furthermore, the effect of pressure on none of the alkali metals was known; it is just here that the largest effects would be expected and the most significant results for theory. The extension of the measurements to these substances demanded certain changes and improvements in the technique. I was soon able to make measurements on the alkali metals, and to my very great surprise found that the resistance of lithium increases under pressure, whereas that of the other alkali metals sodium and potassium decreases greatly. It was obvious that our pictures of the mechanism of conduction are not yet so perfect that we can reason by analogy even from one element to another closely related in the periodic table. The importance of making actual measurements on as many of the elements as possible, particularly the rarer ones, was obvious.

In the present work I have therefore attempted to extend the previous measurements to as many new elements as the new resources of my technique, and the availability of the elements themselves has made possible, with especial reference to the question of the resistance of the metals liquid within a moderate temperature range. Furthermore, a number of commercial alloys have been employed in other work, and rough measurements of the effect of pressure on the resistance of them have been necessary; it has been an easy matter to make the measurements precise enough to be included here. Of course the entire question of the effect of pressure on the resistance of the alloys is a most complicated one, and these isolated results cannot as yet have much significance.

The results given here are for eighteen new elements and six commercial alloys. In addition, better results than were possible in the previous work are here given for tungsten and magnesium. Better results on tungsten were possible because of the availability of purer material, and for magnesium the new technique makes possible the elimination of contact resistance, which introduced very large error in the previous work.

Experimental Method.

The metals measured in the previous investigation could all be made into wire of small diameter, and therefore high resistance, and nearly all of them could be soldered. The resistance was measured on a Carey Foster bridge. It was essential to accuracy that the resistance be so high and the contacts so good that the relative changes in contact resistance under pressure were negligible. Very few of the metals of this investigation satisfy this condition. For the measurement of the effect of pressure on the resistance of these, some sort of potentiometer method is indicated. The resistance of the contacts then is without effect, and relatively small changes on small resistances can be measured accurately.

The application of a potentiometer method demands four leads to the pressure chamber, two current leads, and two potential leads. Three of these leads must be insulated from the pressure chamber; the fourth may be grounded on the walls. An insulating plug carrying three leads was used in this work. It is an obvious modification of the single terminal plugs previously used. It may be mentioned that the modification of the design of the plug suggested on page 641 of the paper referred to, making possible the use of the ring packing, has been in use now for a number of years, and was used with the new three terminal plug. The chief difficulties encountered in the three terminal plug were the mechanical difficulties of securing the accuracy required in getting three terminals into a small space. The fine insulated stems were made of piano wire 0.032 inches in diameter, held into a head at the top by a special wedge grip. Each of these stems with its head was tested before assembling with a tension of 270 pounds, corresponding to a pressure of over 20,000 kg/cm^2. Without a preliminary test there is danger that the stem will pull out of the head under pressure. The mica washers used for insulation of the plug were punchings, made a tight fit for the hole, which was 0.209 inches diameter. They were forced into place in the plug, and drilled concentrically for the stem with suitable jigs after they were in final position. Later the mica washers have been replaced with pipe-stone washers with more satisfactory results. The chief difficulty encountered with this plug has been in using it near 100°. Here the rubber insulation gives out under the action of the petroleum ether with which pressure is transmitted, and the insulation has to be renewed much more frequently than with the larger plug.

The method of electrical measurement is a null substitution method. In series with the material under pressure is a second resistance, part of which consists of a slide wire. By means of a variable slider, it is possible to tap off a variable part of this second resistance. A throw-over switch enables either the potential terminals of the pressure coil or the variable part of the series resistance to be connected to the indicating galvanometer. This galvanometer is a Leeds and Northrup high sensitivity moving coil instrument. At the scale distance used its sensitiveness was 10^{-9} volts; its sensitiveness could be decreased with appropriate shunts.

The measurements are made by adjusting the various resistances so that there is no change of deflection on operating the throw-over switch. The resistance of the pressure coil may then be computed from the known values of the other resistances. In practise, sensitiveness and speed of operation are increased by throwing into the galvanometer circuit another e.m.f. approximately equal and opposite to the potential difference across the pressure coil, so that the actual deflection is approximately zero. This balancing e.m.f. should be variable over a wide range and should be fairly constant. To produce it, I used the apparatus previously used in measuring thermal e.m.f. under pressure, tapping across the former pressure terminals. The refinements of that apparatus were not necessary, but it was easier to use apparatus already at hand than to construct new. The apparatus by which the variable balancing e.m.f. was applied is indicated by VE in Figure 1.

The details of the connections are shown in Figure 1. When adjustments are made we know that the potential drop around R (the pressure coil, which is usually a small fraction of an ohm) is equal to that about R_3 plus r_1. This latter drop of potential may be computed from the known values of R_1, R_2, R_3, r_1, and r_2, and gives

$$R = \frac{R_1(R_3 + r_1)}{R_1 + R_2 + R_3 + r_1 + r_2}.$$

The resistance r_1 (and r_2 accordingly) is the only resistance varied during a pressure run; the other resistances R_1, R_2, and R_3 being appropriately chosen and then kept constant during each run. Since $r_1 + r_2 = r$ (a constant) we have, for any one run,

$$\Delta R = C\,\Delta r_1$$

or, putting $R = R_0 + \Delta R$, and writing r_{10} for the initial value of r_1 corresponding to $R = R_0$

$$\frac{\Delta R}{R_0} = \frac{\Delta r_1}{R_3 + r_{10}} = \frac{\Delta l}{L_3 + l_0'}$$

where L_3 is the length of the slide wire having the resistance R_3, and l_0 and Δl are the actual readings of the slide wire. This arrangement therefore, gives immediately in terms of slide wire settings the proportional change of resistance under pressure. If R_3 is kept constant for the runs on the same metal at different temperatures, making the necessary adjustments in passing from one temperature to another by changing only R_1 and R_2, the readings give directly a comparison of the pressure coefficients at different temperatures without demanding a knowledge of how the resistance itself varies with temperature. This was the procedure followed in this work; the pressure coefficients

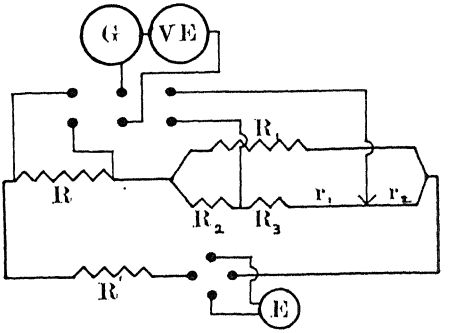


FIGURE 1. The electrical connections by which resistance is measured. The resistances are so adjusted that the potential drop across R is equal to that across $R_3 + r_1$.

are therefore independent of any error in the temperature coefficient of resistance at atmospheric pressure.

In actual construction, all parts practical were made of copper. The resistances R_1 and R_3 were fixed coils dipping in mercury cups in $\frac{3}{4}$ inch copper bars. The apparatus was so designed that all terminals were within a few inches of each other, in order to avoid thermal effects. The slide wire was of manganin. The slider was also of manganin, and was attached by soldering to a flexible many-stranded manganin wire making connection at the other end to a copper block surrounded by the bars containing the other terminals. By soldering the flexible manganin lead to the slider very close to the point of contact with the slide wire, thermal electromotive forces in this part of the circuit were very largely avoided.

The effect of parasitic electromotive forces in the circuit was eliminated by taking the mean of readings with direct and reversed potentiometer current. A reversing switch was supplied for this purpose, as also in the circuit of the balancing variable e.m.f. The only requirement in the potentiometer current is that it shall remain constant during the substitution of the pressure coil for the slider. The substitution was made rapidly by a double throw switch, so that an ordinary dry cell was entirely good enough as the source of the potentiometer current.

The function of the resistance R^1 (Figure 1) was merely to provide an additional adjustment by which the deflection of the galvanometer might be easily made null. An ordinary decade box was good enough for this.

The usual procedure was as follows. A preliminary examination indicated the order of the pressure effect. R_3 was then so chosen that the motion of the slider would be of the order of 10 cm. for the entire pressure range, the total length of the slide wire being 60 cm. R_1 and R_2 were then so chosen, depending on the actual resistance of the pressure coil, that the galvanometer deflection was unaltered on substituting the pressure coil for the slide wire. The following coils for R_1 and R_3 usually gave sufficient range of choice; two 0.5 ohm coils, two 1's, and one each of 2, 3, 4, 10, 20, and 30 ohms. For R_2 a plug box from 0.1 to 1000 ohms was used. R^1 was then set at about 2000 ohms, or less if the parasitic e.m.f.'s. were troublesome, and the balancing e.m.f. adjusted to give no deflection. These adjustments were preliminary to the application of pressure. The adjustments after each change of pressure were, first, an adjustment of R^1 to give again approximately null deflection when the pressure coil is in circuit, second, setting of the slider to give no change in deflection on substitution, third, reversal of the potentiometer current and the balancing e.m.f. and resetting of the slider for no change of deflection, and fourth, change of the potentiometer current and the balancing e.m.f. back to their original directions and again setting the slider. By taking an odd number of readings the effect of any slow change of the parasitic e.m.f. due to dissipation of the heat of compression was eliminated. The potentiometer current was usually so chosen that the difference of slider setting for the two directions of the current occasioned by the parasitic e.m.f. was less than 1 cm.

The coils were all compared with standards and proper corrections applied. The slide wire was calibrated and corrections applied for lack of uniformity. In general, all the precautions of manipulation

and construction previously employed in measurements of resistance or thermal e.m.f. under pressure were observed here also.

The methods of computation were essentially the same as those which have been described in great detail in the previous paper. Any slight modifications were entirely obvious, and it is not necessary to describe them further.

A description in detail of the results obtained for the separate substances now follows.

Detailed Data for Individual Substances.

Lithium. Two distinct series of measurements were made on this substance, at two different times. The first series was on the pressure coefficient of the solid, in the spring of 1919. It was found that the pressure coefficient is positive, and large. This result was so surprising in view of the high compressibility of the metal, and its close relation to sodium and potassium, both of which have a very high negative coefficient, that a correlation of this positive coefficient with other properties of lithium was desirable. For instance, does lithium expand in freezing, like bismuth, and if so, is this connected in any way with the positive coefficient? But on looking up the data I could not find that the melting data for lithium had ever been determined. It was not even known whether lithium expands or contracts on melting. The second series of measurements, in the winter of 1919-20, was concerned with the effort to obtain some of the missing data. In particular, it was desirable to find the volume relations on melting, and to find whether the pressure coefficient of the liquid is positive as well as that of the solid. I had already found that the positive coefficient of solid bismuth changes to negative on melting.

The first series of measurements, on the resistance of the solid, was made on lithium from Merck, prepared a number of years ago, but kept under oil in sealed glass since then. A chemical analysis by Mr. N. S. Drake showed 0.7% Al, and a trace of Fe. Sodium, if any, could not be determined because only one gram of the lithium was available for analysis. The method of preparation by electrolysis should not allow much impurity of sodium if ordinary care is exercised.

The lithium was extruded cold through a steel die into wire 0.030 inches in diameter, and wound bare onto a bone core. Connections were made at the ends with spring clips. So far as I am aware, no previous measurements have been made on the properties of bare

lithium wire, but because of danger of oxidation, the lithium has been usually enclosed in a glass envelope. Measurements in glass, such as that of temperature coefficient of resistance for example, are not entirely free from objection, because of the constraining action of the glass walls. The error introduced by effects of this sort is presumably not large, but it is nevertheless gratifying to be able to avoid it.

A somewhat special technique is necessary to handle the bare wire successfully. It must, of course, be protected at all times from direct contact with the air. This was accomplished at first by extruding it directly into melted white vaseline, and winding it directly from the pot of vaseline onto the bone core, which was mounted for slow rotation by hand. The wire, in passing from the pot of vaseline to the bone core, becomes covered with a capillary film of vaseline, which rapidly solidifies in the air, forming a perfectly protecting coating. Later, however, the vaseline was replaced with a mixture of "Nujol," which is a carefully refined heavy hydrocarbon, prepared by the Standard Oil Co. and sold as a remedy for constipation, and refined paraffine, melted together in such proportions as to have about the consistency of vaseline. This mixture was suggested to me by Dr. Conant of the Chemistry Department. This change was made necessary by the chemical action of the vaseline. The vaseline of commerce is not a substance of standardized properties; the first can of vaseline which I tried was without appreciable chemical action, but the second was unpleasantly corrosive in its action. The mixture of Nujol and paraffine was much more satisfactory, the lithium remaining bright for days.

The liquid transmitting pressure must also be chosen with care in order to avoid chemical action. At first I used commercial kerosene which had been standing in contact with sodium for several weeks. This was not satisfactory, however, the kerosene gradually turning yellow at room temperature in contact with the sodium, and at higher temperatures the reaction is much accelerated. The transmitting medium finally used was a mixture of Nujol and "petroleum ether" in different proportions, depending on the temperature of the work. At 0° nearly pure petroleum ether must be used in order to avoid freezing under pressure. Another source of chemical action, besides the transmitting medium, is the bone core on which the wire is wound. It is necessary to drive the water as completely as possible out of the core by prolonged heating to 130° or so, but under these conditions the bone becomes very brittle and must be handled with extreme care. Even after every precaution had been taken, some chemical action still

remained. The action tends to cease at the higher pressures. Error from chemical action was eliminated as far as possible by taking the means of readings with increasing and decreasing pressure, and at the higher temperatures by never releasing the pressure to atmospheric, but obtaining the zero reading from an extrapolation of the readings at higher pressures, where the chemical action is slower. The technique in handling sodium was the same as that used for lithium. It is a curious fact that although the chemical action of the mixture of Nujol and paraffine at atmospheric pressure is considerably less on the lithium than on the sodium, at higher pressures the reduction of the action is considerably greater in the case of sodium, so that the zero shift after a run at higher pressures and temperatures was greater in the case of lithium than sodium.

Runs were made on the effect of pressure on the resistance of the bare wire at 0°, 25°, 50° (partial run), 75°, and 96°. The difference between readings with increasing and decreasing pressure decreased uniformly from zero to the maximum pressure, instead of being almost entirely confined to the zero reading, as was the case with sodium. The zero shifts were 7% of the total effect at 0°, 5.5% at 25°, 7.8% at 75° and 18% at 96°. The run at 50° was not completed because of accident. In spite of the large zero shifts, the mean of the readings with increasing and decreasing pressure ran smoothly, and should be only little affected by the chemical action.

The temperature coefficient of resistance at atmospheric pressure was obtained from a coil of bare wire similar to that of the pressure measurements. In order to avoid as much as possible the effect of chemical action, four thermostats were kept running simultaneously at 0°, 25°, 50°, and 75°. The coil was immersed in a well of Nujol which had previously come to the temperature of the bath. After a reading at one temperature the coil was transferred in a few seconds to the bath at the next temperature, and readings made after a fixed constant interval. Seventeen minutes proved to be sufficient for acquiring complete thermal equilibrium. Readings were made successively from 0° to the maximum and back to 0° again. The mean of the ascending and descending readings should be free from error from chemical action. The zero shift after the run was 2.8% of the total effect, against 5.4% for sodium. The average coefficient between 0° and 100° was 0.00458. Bernini [2] found for lithium in glass the mean value 0.00457 between 0° and 177.8°. He found the relation between temperature and resistance to be linear. I found the resistance to increase more rapidly at the higher temperatures;

this would mean an average coefficient between 0° and 177.8° even larger than 0.00458.

The independent pressure runs at different temperatures did not fit as smoothly together as they frequently do, but the pressure effect varied irregularly from one temperature to another. Within the limits of error a dependence of pressure coefficient on temperature could not be established, and in the finally smoothed results the pressure coefficient is assumed independent of temperature. This demanded a maximum readjustment of the observed readings of 2.0% at 75°.

TABLE I.

RESISTANCE OF LITHIUM.

Pressure kg/cm²	Resistance 0°	25°	50°	75°	100°
0	1.0000	1.1044	1.2122	1.3280	1.4580
1000	1.0069	1.1120	1.2206	1.3372	1.4681
2000	1.0140	1.1199	1.2292	1.3466	1.4784
3000	1.0212	1.1278	1.2379	1.3561	1.4889
4000	1.0285	1.1359	1.2468	1.3655	1.4996
5000	1.0360	1.1442	1.2558	1.3758	1.5105
6000	1.0436	1.1525	1.2651	1.3859	1.5216
7000	1.0514	1.1612	1.2745	1.3963	1.5329
8000	1.0594	1.1700	1.2842	1.4069	1.5446
9000	1.0675	1.1789	1.2940	1.4177	1.5564
10000	1.0757	1.1880	1.3039	1.4285	1.5683
11000	1.0841	1.1973	1.3142	1.4397	1.5806
12000	1.0927	1.2068	1.3246	1.4513	1.5932

Average coefficient 0 to 12000 kg. + 0.0₅772.
This coefficient is independent of temperature.

The values of the resistance of the solid at 25° intervals of temperature and 1000 kg. intervals of pressure are shown in Table I. The pressure coefficient is seen to be positive, as already noted. Furthermore, the pressure coefficients, both instantaneous and absolute, increase with increasing pressure. This we would not expect, but it seems to be the normal type of behavior for substances with positive coefficient.

The second series of measurements was made with another sample of lithium, much larger in amount, which I obtained through the kind-

ness of Dr. A. W. Hull of the Research Laboratory of the General Electric Co. The purity was not known. It was prepared by electrolysis of the fused chloride with graphite electrodes; the chloride was pure, so that any impurities were introduced in the electrolysis. There were inclusions in it of some slag-like substance which had to be cut out as well as possible. This specimen was used for a determination of the melting curve. The method was that of the discontinuity of volume, which I have previously used in determining melting or transition curves, and has been fully described elsewhere.[3] The volume of the specimen was about 5 c.c. It was placed in an iron container, and pressure transmitted to it with Nujol. It was evidently somewhat impure, for the corners of the melting curve were

TABLE II.

MELTING CURVE OF LITHIUM.

Pressure kg/cm²	Temperature
0	178.4°
1000	182.1
2000	185.5
3000	188.8
4000	191.8
5000	194.6
6000	197.1
7000	199.4
8000	201.6

considerably rounded, melting being detectible at least 1000 kg. before the end of melting. This corresponds to a spreading of melting at constant pressure over a temperature range of 3.5°. What the depression of the freezing point is at the conclusion of melting, that is, how much the observed curve should be raised in order to correct for the impurity, it is not possible to state from the data. Points on the freezing curve were obtained at three temperatures. A curve was drawn through these points and the data from the smooth curve are given in Table II. The curve and the observed points are also shown in Figure 2. The points lie on the curve as drawn, but it is seen that there may be some uncertainty about the extrapolation to atmospheric pressure. The value of the melting temperature at atmospheric

pressure given in the Table was extrapolated from the three observed points on the assumption that $\frac{d^2\tau}{dp^2}$ is constant.

The most important result of these melting observations is that the melting curve is normal, pressure and temperature rising together. This means that the solid contracts on freezing, as is normal. The positive pressure coefficient of resistance of the solid therefore need not be due to the peculiar mechanism that it is in the case of bismuth.

The changes of volume on melting are very small, and because of the rounding of the corners, very hard to determine accurately. The error was too great to establish any regular variation of the change along the melting curve. The best mean value for the fractional increase of volume on melting is 0.006.

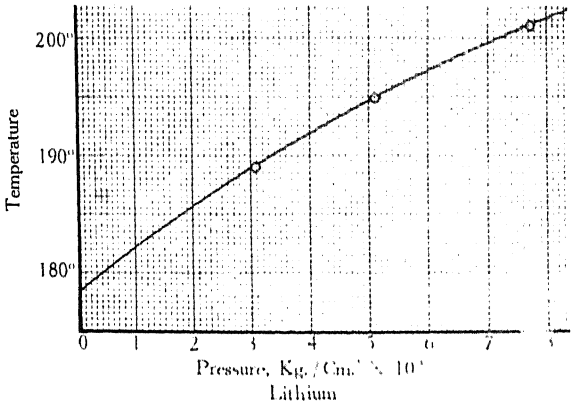


FIGURE 2. The melting curve of lithium.

The effect of pressure on the resistance of the liquid was measured on the same sample as that of the melting curve, the sample from Merck having been used up by the chemical analysis. Considerable difficulty was met in devising a suitable method. It is well known that melted lithium attacks glass, and this I verified by my own experience. Previous experimenters have been able to measure the resistance of the liquid in a glass capillary by protecting the interior surface of the capillary with a film of oil. This introduced error because of the space occupied by the film of oil, and is not adapted to use under pressure, the oil film being penetrated after a few compressions. The method finally adopted was to surround the lithium with

a capillary of an alloy of high specific resistance, which is not attacked by the lithium. For this purpose I used the allow known under the trade name of "№ 193 Alloy," manufactured by the Driver Harris Co. The specific resistance is about 50 times that of copper. I succeeded in drawing this into a fine capillary 0.045 inches outside diameter, and 0.032 inside diameter. An attempt to treat Nichrome similarly did not meet with such ready success, it being much harder to draw. The capillary was plugged at one end with a pin of iron, and at the other end an iron cup was silver soldered, no silver solder coming in contact with the lithium. Four copper leads were soldered to the outside of the capillary, two at each end, for use as current and potential leads, and the resistance was measured in the regular way by the potentiometer method. The capillary was filled by melting the lithium into it in vacuum. The resistance of the capillary was from five to ten times the resistance of the lithium which filled it, varying with the pressure and temperature. Preliminary measurements were made on the resistance of the capillary when empty, and on its temperature and pressure coefficients. These values for the capillary are given for themselves under the heading № 193 Alloy. The temperature and pressure coefficients are both small compared with those of lithium.

The capillary and the lithium inside it constitute two resistances in parallel. The various resistances are connected by the relation

$$\frac{1}{R_0} = \frac{1}{R_c} + \frac{1}{R_L}$$

where R_L is the resistance of the lithium filling the capillary, R_c is the resistance of the capillary alone, and R_0 is the observed resistance of the capillary and lithium in parallel. By differentiating this expression with respect to the pressure we obtain

$$\frac{1}{R_L}\frac{dR_L}{dp} = \frac{R_L}{R_0}\left(\frac{1}{R_0}\frac{dR_0}{dp}\right) - \frac{R_L}{R_c}\left(\frac{1}{R_c}\frac{dR_c}{dp}\right).$$

From the pressure coefficient as observed, and the pressure coefficient of the capillary separately determined, it is therefore possible to obtain the pressure coefficient of the lithium alone which fills the capillary. The term involving the pressure coefficient of the capillary is seen to be small, so that this coefficient need not be known with great accuracy, and the ratio of the resistance of the lithium to the observed resistance may be found with any accuracy desired, so that

the results should not have appreciably any larger error than the observed resistances themselves.

It is obvious that the temperature coefficient of resistance may be found in a way precisely similar to the pressure coefficient.

Readings were made on the resistance of the liquid as a function of pressure at 202.5° and 237.4°. The pressure range of the lower temperature run was 8000 kg., since the melting curve restricts the domain of existence of the liquid, but at the higher temperature the pressure range was the entire 12000 kg. In order to avoid chemical action as far as possible, pressure was not released entirely to zero, but the minimum was about 1000 kg., and the results were extrapolated to zero. Measurements were also made on the solid at 171.6° to 8000 kg. (pressure was not raised higher for fear of distorting the capillary), and on the resistance of the solid as a function of temperature at atmospheric pressure down to 0°.

The most important result is that the pressure coefficient of the liquid is positive like that of the solid, reversing the behavior of bismuth. At the two temperatures the relation between pressure and resistance was linear within the limits of error of the measurements. At the lower temperature the maximum departure of any observed point from a straight line was 2% of the total effect, and at the higher temperature it was 1.3%. The coefficient is $+ 0.0_5927$, independent of temperature to the last figure. The coefficient of the liquid is seen to be slightly larger than that of the solid. The correction for the capillary brought the observed value from 0.0_5700 to 0.0_5927.

The temperature coefficient of the liquid, corrected for the capillary, was such as to give between 202° and 237° an increase of 0.00145 of the resistance at 202° for every degree rise of temperature. This is less than the reciprocal of the absolute temperature, giving, when multiplied by the absolute temperature, 0.689. The coefficient of the solid was found to be markedly higher than the reciprocal of the absolute temperature. This is again an example of the fact that the temperature coefficient of the liquid is in general less than that of the solid. Bernini [2] found for the liquid between 180° and 200° a coefficient equal to 0.00077 of the resistance at 200°, considerably lower than the value above.

No correction has been applied to the above values for the compressibility or thermal expansion of the capillary, since these are not known. We have seen that the temperature correction is in general slight. If the compressibility of the alloy is the same as that of pure iron, which is a not unplausible assumption, the coefficient of the specific resistance will be about 2% less than the value above.

The pressure coefficient of the solid lithium was measured in the capillary at 171°. The most important result of this measurement was the verification of the positive coefficient. The numerical value of the coefficient cannot be accepted, however, because of the restraining effect of the capillary. A similar effect had already been met in the case of Gallium. The results for the resistance of the solid were very irregular, there being deviations of 10% from the mean curve. The value found for the coefficient was $+ 0.0_4159$, nearly twice the value found at low temperatures for the bare wire. It is quite possible that part of this large difference is real, since we in general expect the coefficient to become larger at the higher temperatures. It was not possible to definitely state any variation of the coefficient within the range 0° to 100° for the bare wire, since chemical action cut down the accuracy of the measurements. It is also possible that some of the difference may be due to difference of the material, this latter specimen not being so pure. The pressure coefficient of the solid in the capillary was also measured at 94°, but the irregularities of the data were much greater than at 171°. One would expect the effect of constraint to become greater farther from the melting point. The best value of the coefficient at 94° was 25% higher than at 171°, but the accuracy was so low that it is not at all certain that there was any real difference.

The temperature coefficient of the solid in the capillary was also measured between 0° and 171°. Here again we should not expect the results to be very accurate because of the effects of constraint. The mean coefficient over this range was 0.0039. This is considerably less than for the unconstrained wire; part of the difference may be due to greater impurity.

The change in the resistance on melting at atmospheric pressure could be computed from the measurements on solid and liquid separately. The specific resistance of the liquid is thus found to be 1.68 times that of the solid at the melting point at atmospheric pressure. The only other published value is by Bernini,[2] who found 2.51. Bernini's value of the melting point was 177.84°, somewhat lower than the value given above, so that it is not probable that the difference is to be ascribed to greater purity of his sample. I also made an attempt to find the variation of the ratio of specific resistance of solid and liquid along the melting curve, but this cannot be very accurate, because of the constraining effect of the capillary. Using the value found for the pressure and temperature coefficients of the solid in the capillary, and assuming that the temperature coefficient is not affected by pressure (which has been proved to be true by direct measurement in most

cases), the resistance of the solid was extrapolated to the melting curve at 202.5° and 8430 kg., and at this point the ratio of resistance of liquid to solid found to be 1.49. The accuracy is not high, and probably the only conclusion justified is that the change of the ratio along the melting curve is not large.

Sodium. The material was from the same sample as that previously used in determinations of the change of melting point under pressure.[4] No chemical analysis has been made, but the sharpness of the melting is evidence of the high purity. Two series of measurements of the resistance were made. The first, in the spring of 1919, was on the resistance of the solid below the melting point at atmospheric pressure. The second series, in the fall and winter of 1919-20, was on the resistance of both solid and liquid at temperatures above 97.6°.

For the measurements of the resistance of the solid below 97.6° the sodium was extruded into wire through a steel die, and the wire wound bare on a bone core. As in the case of Lithium, I am not aware that measurements have been made previously on the resistance of the bare wire, but the material has been enclosed in a glass envelope. The details of manipulation were essentially the same as for lithium, except that sodium is much softer, and consequently harder to handle. Two sizes of wire were used, at first 0.015 inches in diameter, and later 0.030. The larger size is considerably easier to handle, and the resistance is high enough to give the requisite accuracy. The initial resistance was of the order of 0.5 ohms for the small wire, and 0.2 ohms for the larger wire. Connections were made to the sodium wire with spring clips, as with lithium. The springs were helical springs of piano wire, 0.009 inches diameter, wound on a mandrel 0.06 inches diameter. The springs were pulled out so as to separate the spires, and the sodium wire dropped in between the spires. The wire was protected between the spires by wrapping round it a covering of gold or silver foil 0.001 or 0.002 inches thick; otherwise the soft wire is pinched off by the spring. Due to chemical action, the resistance at the spring contacts sometimes became so high as to make trouble. Contact could always be restored by passing through the contact a current from a small magneto.

Experiments were made on six different samples before a complete set of readings was obtained. Repetitions were necessary because of the effect of corrosion, and also because of accidents to the insulation of the three-terminal plug. In addition to complete runs at 0°, 25°, 50°, and 75°, one fragmentary run was made at 0°, and three at 50°.

These fragmentary runs have been given due weight in the final results.

No preliminary pressure seasoning of the wire was attempted. This is usually unnecessary for soft metals, and in this case was undesirable because of the effect of chemical action. The amount of chemical action may be estimated from the amount of the change of the zero after a run. At 0° the zero change was 5.6% of the total pressure effect; at 25° 8.1%; at 50° 1.9%, and at 75° at 1000 kg. 4.7%. The smaller effects at 50° and 75° are because the Nujol mixture was used at these temperatures to transmit pressure instead of kerosene. Since the readings with increasing and decreasing pressure were made at uniform time intervals, the mean zero should contain little error from corrosion. Aside from the zero displacements, the points at high pressures lay very regularly on smooth curves. At 0° the greatest departure of any point from a smooth curve was 1.6%; at 25° 1.3%, at 50° 0.8%, and at 75° 1.0%.

The final results were obtained by first smoothing independently the results at each temperature, and then smoothing the runs at each temperature so as to give smooth temperature differences. The maximum adjustment in this temperature smoothing was at 50° and 3000 kg., where an increase in the observed readings of 1.2% of the total effect was necessary.

The temperature coefficient at atmospheric pressure was obtained from a coil of bare wire similar to that of the pressure measurements. The details of the measurements were exactly the same as for lithium. The two readings at 0° differed by 5.4% of the total temperature effect. The relation between temperature and resistance can be expressed by a second degree equation in the temperature. The results at even temperature intervals are included in Table III. The resistance of the solid at 100° (melting point 97.62°) may be extrapolated from readings between 0° and 75° and gives as the average temperature coefficient between 0° and 100° 0.005465. Northrup [5] gives for the temperature coefficient of sodium in glass the value 0.0053, obtained by a linear extrapolation of values between 20° and 93.5°. Bernini [6] gives for the same temperature range (0° to 100°) 0.00428. As already remarked, there seem to be no previous values on the unconstrained metal.

The measurements on the resistance in the domain of both liquid and solid above 97.6° were made with the sodium enclosed in a glass capillary. The details were exactly the same as for potassium. In point of time the measurements of potassium were made first, and the

TABLE III.

RESISTANCE OF SODIUM.

Pressure kg/cm²	0°	20°	40°	60°	80°	100°	120°	140°	160°	180°	200°
0	1.0000	1.0950	1.1971	1.3078	1.4227	2.2381	2.3835	2.5399	2.7054	2.8849	3.0725
1000	.9376	1.0248	1.1184	1.2168	1.3196	1.4257	2.184	2.326	2.476	2.639	2.808
2000	.8830	.9644	1.0513	1.1411	1.2340	1.3283	2.018	2.147	2.283	2.433	2.580
3000	.8348	.9192	.9926	1.0762	1.1608	1.2451	1.877	1.995	2.120	2.257	2.397
4000	.7924	.8647	.9409	1.0192	1.0971	1.1739	1.226	1.866	1.982	2.106	2.235
5000	.7550	.8235	.8955	.9692	1.0419	1.1123	1.147	1.755	1.861	1.975	2.092
6000	.7218	.7865	.8547	.9240	.9926	1.0590	1.077	1.178	1.755	1.861	1.968
7000	.6922	.7538	.8183	.8844	.9495	1.0118	1.017	1.112	1.662	1.758	1.857
8000	.6658	.7243	.7862	.8492	.9100	.9695	0.964	1.053	1.578	1.667	1.758
9000	.6422	.6980	.7569	.8167	.8758	.9320	0.917	1.002	1.505	1.588	1.670
10000	.6211	.6741	.7305	.7878	.8443	.8986	0.875	0.956	1.033	1.517	1.593
11000	.6022	.6528	.7070	.7618	.8163	.8690	0.841	0.919	0.991	1.455	1.525
12000	.5854	.6332	.6854	.7381	.7908	.8425	0.810	0.885	0.954	1.401	1.464

description of the capillary and the method of filling it will be found under potassium. Seven runs were made with the sodium in glass, with several different capillaries. These runs were at 134.0°, on both solid and liquid, at 143.6° on the liquid only, at 163.1° on the liquid only, at 165.0° on both liquid and solid, and at 171.8°, 197.1° and 198.1° on the liquid only. In addition, readings were made at atmospheric pressure from which the change of resistance on melting and the temperature coefficient of resistance of the liquid could be obtained. These runs were of varying degrees of excellence. Those at 165° and 197° showed zero shifts of only 0.5% and 0.3%, and were given the greatest weight in computing the resistance of the solid. In general the observed points lay very smoothly, and there was little difference between the results with increasing and decreasing pressure, indicating little direct effect due to the constraint exerted by the walls of the capillary.

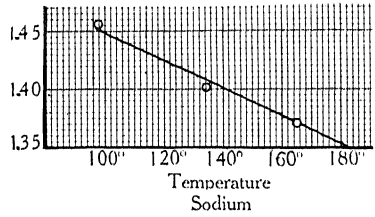


FIGURE 3. The ratio of the resistance of liquid to solid sodium as a function of temperature along the melting curve.

The ratio of resistance of liquid to solid was observed at three temperatures; the observed points are shown in Figure 3. The ratio decreases somewhat with increasing pressure and temperature along the melting curve. In reducing the observed values to smoothness, it was assumed that the ratio varies linearly with temperature, and is given by the line shown in the figure.

The values of resistance as a function of pressure and temperature from 0° to 200° and to 12000 kg. are shown in Table III. This table falls into two parts; the first part, including the values through 100°, are relative values of the "observed" resistance, being derived from measurements on the bare wire. Above 100° the values listed are relative values of the specific resistance, the observations having been made on the sodium in a glass capillary, and corrections applied for the compressibility and thermal expansion of the glass. For the

linear expansion the value 0.038 was assumed, and for the cubic compressibility Amagat's figure 2.2×10^{-6}, with his temperature coefficient of compressibility of 10% for 100°. In order to reduce the part of the table below 100° to relative specific resistances or that above 100° to relative "observed" resistances, it would have been necessary to have known the compressibility of sodium over this range of pressures and temperatures, and this has not yet been determined experimentally. From the differences of the pressure coefficients in the two parts of the table, however, it is possible to get some idea of the magnitude of the compressibility. Thus it will be found that the mean coefficient of "observed" resistance between 5000 and 12000 kg. at 100° becomes consistent with the mean coefficient of specific resistance over the same range if the compressibility is 0.00002. Richards found for the initial compressibility at 20° the value 0.000015. The difference between these two values does not mean an impossibly large temperature effect.

In Figure 4 the isothermals of resistance against pressure have been drawn for a number of temperatures. The values are taken from the table and have the same discontinuity at 100° as the values of the table. In fact, this discontinuity is quite evident in the figure. The change of resistance with pressure is seen to be large, larger than for any other metal which I have measured except potassium. Under 12000 kg. the change of resistance of the solid is of the order of 40% of the initial resistance. The mean coefficient of the liquid is larger, the decrement being about 50% for the same pressure range. The initial coefficient of the liquid varies little with temperature, but the initial coefficient of the solid increases markedly with rising temperature.

The pressure coefficient of resistance of sodium has not been previously measured, so there are no other values for comparison, but other observers have measured the temperature coefficient of solid and liquid and the ratio of resistance of liquid to solid at atmospheric pressure. The values of Northrup and Bernini for the coefficient of the solid have been already quoted. It is to be noticed that the values of Northrup and Bernini are for the specific resistance, since their materials were enclosed in a rigid container, whereas my coefficient is of the "observed" resistance, and was obtained on the bare solid. The coefficient of specific resistance is greater than that of "observed" resistance by the linear expansion. Taking as the linear expansion of sodium 0.000069, my value of the coefficient of the "observed" resistance would give 0.00552 for the coefficient of the specific resistance. This value is seen to be much higher than that

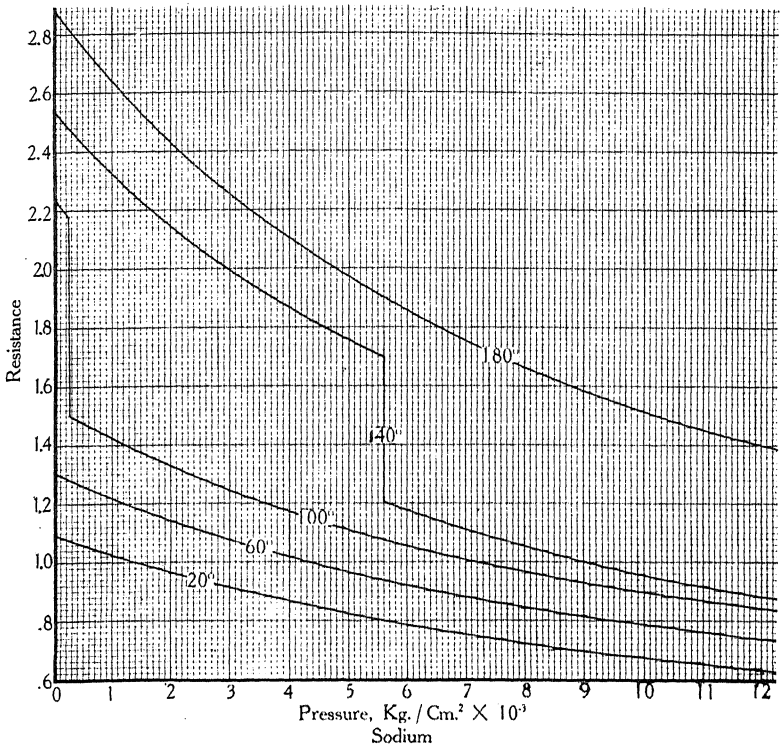


FIGURE 4. Relative resistances of sodium at constant temperature as a function of pressure.

of Bernini, and appreciably higher than that of Northrup. Doubtless the freedom from constraint of the bare wire is in large part responsible. As the solid sodium expands in the glass container it will exert a pressure on the walls, which will have the effect of decreasing the resistance, and making the temperature coefficient appear too low.

For the temperature coefficient of the liquid, Bernini [6] found between 100° and 110° 0.00279 of the resistance at 100°. Northrup's [5] mean value between 100° and 140° is 0.00330 of the resistance at 100°. My mean value between 100° and 120° is 0.00325, slightly lower than the value of Northrup. It is not yet established whether the purer liquid metal usually has a higher temperature coefficient than the impurer or not.

For the ratio of the resistance of liquid to that of solid at the melting point Bernini found 1.337, and Northrup 1.44. The value which I found above was 1.451, in good agreement with that of Northrup. The agreement of my high pressure values with that found at atmospheric pressure makes it probable that in my work the formation of cavities did not cause any essential error at atmospheric pressure.

It will be noticed that throughout, my values are considerably closer to those of Northrup than Bernini. It is probable that in spite of his efforts, Bernini did not succeed in eliminating the effect of cavities, or that there was some other source of consistent error.

POTASSIUM. Material from the same lot was used as that used previously for the measurements of the coördinates of the melting curve.[4] The purity was high, as shown by the sharpness of freezing. Resistance measurements under pressure were made on both the liquid and the solid. The mechanical softness of potassium, and its much greater chemical activity made it infeasible to use the solid in the form of bare wire, as had been possible with sodium and lithium. The metal had to be contained, therefore, in a glass capillary. This is to be regretted, but its much greater softness makes any error introduced by the restraining action of the glass much less than in the case of the other metals. Special examination was made of the magnitude of the error introduced in this way by measuring the difference between the resistance under increasing and decreasing pressure at 28°. Very noticeable differences between the ascending and descending curves were found, corresponding to a maximum difference of mean pressure in the metal and the surrounding liquid of 100 kg. The maximum discrepancy occurred at the highest pressure, where it would be expected that the viscosity of the metal would be the greatest. The pressure difference of 100 kg. was estimated from the differences of resistance, assuming that the stresses in the metal had the same effect on resistance as a hydrostatic pressure. Of course there actually were stresses in the metal of a shearing nature, and it is exceedingly unlikely that the effect of such stresses is equivalent to a hydrostatic pressure, so that it is probable that the glass capillary was called on to support a stress difference of considerably more than 100 kg. The mean of readings with ascending and descending pressure were taken as the correct value. There were, however, considerable irregularities, doubtless due to the irregular response of the glass capillary to the heterogeneous strains in it. At higher temperatures the differences between the readings with ascending and descending pressure became much less than at 28°, as one would expect, but it was

evident that some of the irregularities remained at all temperatures. In view of the probably much greater magnitude of the effect at still lower temperatures, no readings were attempted at temperatures lower than 28°.

The capillary containing the potassium was in the form of a U, with open cups at the two ends. Into each cup, two fine platinum wires were sealed for the current and potential leads, and measurements were made by the potentiometer method. The capillary was filled by melting the potassium into it in high vacuum. The filling was accomplished by sealing one of the cups, and connecting to the other cup a succession of bulbs communicating with each other through narrow necks. The potassium was placed in the most remote of the bulbs, and the apparatus was exhausted with a diffusion pump, heating the bulbs and capillary to remove occluded gases. The glass was now sealed off from the pump, and the melted potassium run in succession from one bulb to the next. In this way the scum of oxide was removed. Previous work had shown that further purification of this particular specimen of potassium, as by distilling, was superfluous. When the melted potassium reached the cup of the capillary, into which it could not enter because of capillary action, illuminating gas was admitted to the farther bulb, driving the melted potassium before it and thus completely filling the capillary. The seal of the other cup was now broken, and the capillary mounted as soon as possible in the pressure apparatus under Nujol, the open ends of the capillaries being protected from oxidation with Nujol and paraffine paste during mounting.

Five runs were made, with two capillaries. The first filling gave measurements of the resistance of the solid alone at 28.6° and 54.2°. The second filling was used at higher temperatures, 95.7°, 132.2° and 167.0°, and gave measurements on both solid and liquid. For the second set of runs a special apparatus had to be used by which the insulating plug was kept cold in a third cylinder. This was first used in the measurements on liquid bismuth, and will be found described under that metal. The same apparatus was also used in the high temperature measurements on lithium and sodium. In addition to the pressure runs, the same fillings of the capillaries were used to give the temperature coefficient of resistance by varying the temperature at atmospheric pressure.

The resistances as measured were smoothed to uniform temperature and pressure intervals, choosing a temperature interval of 35° as being closest to the greatest number of the actual readings. In this smooth-

ing the irregularities introduced by the glass capillary were apparent. The individual readings seldom showed irregularities of much more than the sensitiveness of the measurements, but there were consistent departures between readings with increasing and decreasing pressure, and consequent uncertainty as to the correct result. Sometimes an adjustment of as much as 2% in the total resistance was necessary to bring the runs for different temperatures into smooth register with each other. Because of the extreme largeness of the coefficient, a change of 2% in the resistance itself usually means a much smaller percentage change in the decrement of resistance. Since it was the decrement which was measured, the actual measured quantities

TABLE IV.

RESISTANCE OF POTASSIUM.

Pressure kg/cm²	25°	60°	95°	130°	165°
0	1.128	1.307	2.387	2.724	3.040
1000	.941	1.079	1.911	2.222	2.568
2000	.799	.911	1.586	1.842	2.176
3000	.692	.786	.880	1.567	1.853
4000	.615	.696	.777	1.346	1.586
5000	.554	.623	.693	1.183	1.374
6000	.503	.563	.624	.685	1.195
7000	.458	.511	.564	.618	1.050
8000	.420	.464	.508	.551	.928
9000	.387	.425	.463	.500	.829
10000	.358	.389	.420	.450	.481
11000	.333	.358	.383	.407	.432
12000	.310	.330	.350	.369	.389

seldom had to be adjusted by as much as 2%. In making the adjustments, the observed temperature coefficients of both solid and liquid at atmospheric pressure was accepted as most probably correct and retained with only immaterial smoothing. Also the observed change of resistance on passing from the liquid to the solid at various temperatures was accepted as essentially correct. With these as fixed data in the table of resistances, the other measured values for the decrement of resistance were adjusted to smoothness with as little change as possible.

The resistances as thus smoothed are shown in Table IV. The

values tabulated are relative values of the specific resistance, taking as unity the resistance of the solid at atmospheric pressure at 0°. The observed values have been corrected for the expansion and compressi-

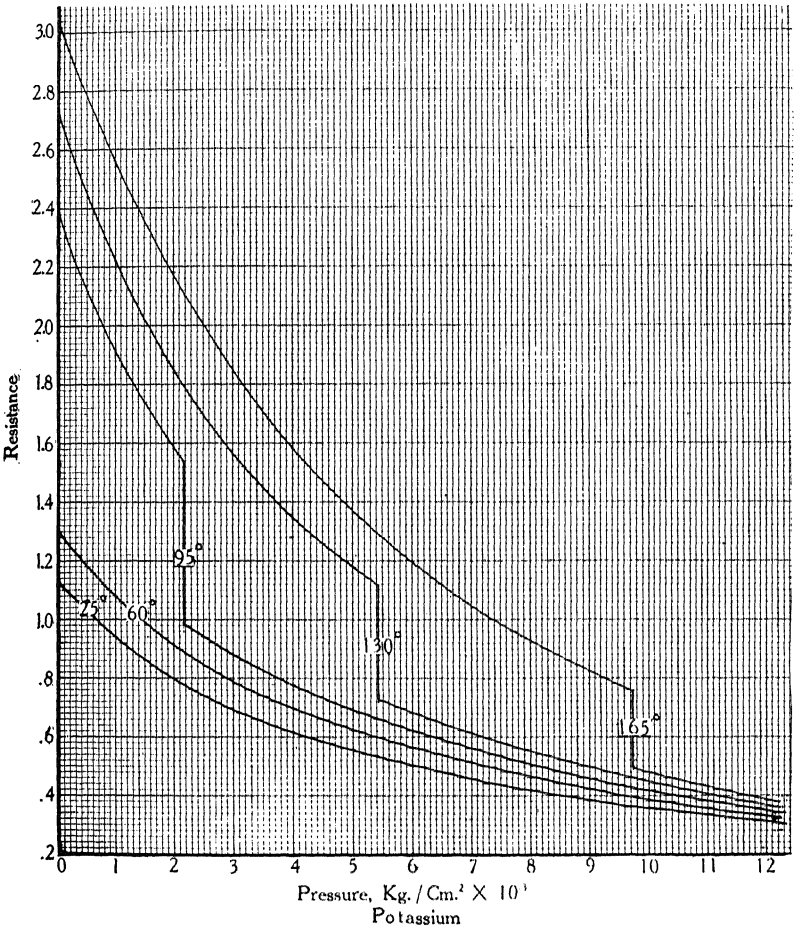


FIGURE 5. Relative resistances of potassium at several constant temperatures as a function of pressure.

bility of the glass, assuming for the linear expansion 0.0_57, and for the linear compressibility 0.0_68. The corrections so introduced are much smaller than usual, because of the very large pressure and temperature

coefficients of this substance. The correction for the thermal expansion of the glass is perceptible as a change of one unit in the last figure in only one part of the table, and the maximum correction for the compressibility is 0.96% of the corresponding resistance. It is to be noticed that the table contains relative specific resistances, and not relative "observed" resistances, as is the case for all metals which are measured in wire form. It is also to be noticed that the table contains the resistances of both solid and liquid; the domain of the solid is separated from that of the liquid by a heavy line.

The data of the table have been plotted in Figure 5. The first and most striking result shown by the table and the figure is the great magnitude of the effect; it is not equalled by any other metal, and is exceeded only by black phosphorus among the substances which I have measured. At 25° the resistance of the solid at 12000 kg. is only 27.5% of its resistance at atmospheric pressure. At the higher temperatures, where change of phase occurs, the resistance at 12000 may be as little as 13% of the atmospheric value. At the melting temperature at atmospheric pressure the coefficient of the liquid is greater than that of the solid, but the coefficient of the liquids shows a quite marked decrease with rising temperature.

TABLE V.

POTASSIUM.

Relative Values of Specific Resistance on the Melting Curve.

Temperature Centigrade	Pressure kg/cm²	Resistance	
		Liquid	Solid
62.5°	0	2.059	1.320
95.0°	2200	1.540	0.990
130.0°	5430	1.128	0.728
165.0°	9710	0.772	0.498

In Table V are shown the resistances, also in terms of the resistance of the solid at 0° at atmospheric pressure as unity, at the melting points. Within the limits of error, the ratio of specific resistance of the liquid to that of the solid at the melting point is nearly independent of the pressure and temperature of melting. The experimental

values found were 1.664 and 1.56 at 62.5° and 0 kg., 1.493 at 95.7° and 2260 kg., 1.550 at 132.2° and 5650 kg., and 1.550 at 167.0° and 10000 kg. The higher of the two values at atmospheric pressure was not satisfactory because the capillary was not filled as well as usual, there being obviously minute cavities between the surface of the metal and the glass, and that result was accordingly discarded. The remaining results show that the ratio is almost exactly constant, and in computing the tables the following values were used; 1.56 at 0 kg. 1.555 at 2200 kg., 1.550 at 5430 kg., and 1.550 at 9710 kg.

The value for the ratio of the resistance of liquid to that of solid at atmospheric pressure may be compared with that of other observers. Bernini [7] has found 1.392, and Northrup [5] 1.53. It is to be seen that my value agrees much better with that of Northrup. This entire question of the ratio of the resistance of the liquid to that of the solid is still in a most unsatisfactory state experimentally, and results by different observers disagree by much more than can be accounted for by errors of measurement or by impurity of the materials. All values with which I am acquainted, both for potassium and other metals as well, have been obtained from measurements of the liquid in a glass capillary, and from measurements of the solid in the same capillary after freezing. The resistance of the solid is without doubt likely to be largely in error because of strains and because of cavities formed during freezing. Matthiesen,[8] in his early work, found discrepancies in measurements of the resistances of the solid of as much as 5% which he traced to this cause. What is more, after the solid has once been formed, and is again melted to the liquid, there may be cavities between the surface of the liquid and the glass. Bernini has found large discrepancies in the resistance of the liquid due to this cause. Furthermore, in most experiments, there has been a film of oil between the surface of the metal and the glass; irregular capillary effects in this film will introduce error. Much of the previous work should be repeated with increased precautions. Measurements on the liquid should be made with a capillary completely filled in vacuum, and the liquid should not be allowed to freeze. The specific resistance of the solid should be obtained from independent measurements of the bare metal, preferably extruded to ensure complete freedom from cavities. Measurements on both solid and liquid should be made over a wide enough temperature range to allow unquestionable extrapolation to the melting point. No measurements should be given much confidence which show premature rounding of the corners of the melting curve. It can now be stated with confidence that all such premature

rounding is due to impurity; in the early days of this kind of measurement there was room for honest question whether the absolutely pure substance would show premature rounding or not.

While it cannot be claimed that the measurements above meet all these requirements, it is evident that any error from cavities must be negligible when freezing takes place under thousands of atmospheres, and as far as purity goes, the potassium used above never showed any preliminary rounding, thus bearing out the observations on the same material on the melting curve. The melting of Bernini's sample was not abrupt, and took place at 62.04°, nearly 0.5° below that of mine. Northrup records the value 63.5° for the melting point of his specimen; this is so high that it seems that it must be due to errors in temperature measurement.

The value which I found for the temperature coefficient of resistance at atmospheric pressure is considerably lower than that of either Bernini or Northrup. The first found 0.00601 between 0° and 50°, and the latter found 0.0058, in terms of the resistance at 0°C., between 20° and 50°. I found the relation to be linear, and the value of the coefficient, corrected for the expansion of the glass, 0.00512 between 0° and 50°. My value for the liquid is, on the other hand, larger than that of Bernini. I find for the mean coefficient between 95° and 130° 0.00403 of the resistance at 95°, and Bernini gives between 90° and 100° 0.00358 of the value at 95°. Northrup's value, reduced to fractional parts of the resistance at 95°, is 0.00342.

In using the Table, caution should be employed not to force it beyond its accuracy. In particular, too much importance should not be attached to the variation of the differences with temperature. If at any time in theoretical work it should be important to know exactly the variations of pressure and temperature coefficients with pressure and temperature for small ranges of pressure, this work should be repeated with apparatus capable of measuring pressures with greater sensitiveness, and the pressures should not be pushed so high as to introduce irregularities in the glass. In this work the smallest pressure steps were 1000 kg., and no readings were made between 0 and 1000 kg. Where the changes are so large in an interval of 1000 kg. it is entirely possible that some essential detail of behavior may have been overlooked, or smoothed out in constructing the Table.

MAGNESIUM. In the previous paper on the resistance of metals under pressure it was possible to give only very rough values for the pressure coefficient of magnesium. Difficulty was previously found in making good connections because of the impossibility of soldering

magnesium and because of the very high resistance of the film of oxide on the surface. With a potentiometer method of measuring resistance, however, this was no longer a difficulty, and accordingly the attempt was made to get more accurate values.

Measurements were made with two samples of magnesium. The first was from the same piece as that on which measurements of resistance and thermal e.m.f. have been already published, and was a contiguous length from the same spool as the e.m.f. sample. It was originally obtained from Eimer and Amend, of commercial quality. The method of manufacture of magnesium, however, is such that impurities are not likely to get into it, and it is a matter of experience that commercial magnesium is of higher absolute purity than most commercial metals. The second sample I owe to the kindness of Dr. MacKay of the Research Laboratory of the General Electric Co. It had been especially purified by him by distillation in vacuum. This was extruded hot to wire of about 0.020 inches diameter, the same in dimensions as the other specimen. Both specimens were mounted in the same way for the measurements, by winding bare on a bone core. Contact was made with spring clips. The resistance at the contacts was so high that error might be introduced because of fluctuations of the potentiometer current, unless the precaution were taken to brighten the wire with sandpaper immediately under the clips just before assembling the apparatus. With this precaution no trouble was experienced from contact resistance.

The measurements on the first sample of magnesium were made just after the apparatus had been constructed, and before all points in the best handling of it had been settled, so that there were a number of incomplete runs. In all, there were ten runs on this sample, five of them complete. The incomplete runs were given due weight in the final results. The maximum deviation of the individual readings from regularity was of the order of 1%. It will not pay to reproduce the results in detail, because this sample was presumably less pure than the second, and the results are somewhat different.

Three runs were made on the second and purer sample, at 0°, 51° and 95°, after three preliminary applications of 3000 kg. at room temperature to season. The results were smoothed and a Table constructed in the regular way. The readings ran regularly. At 0° the zero displacement after the run was 1.6% of the total effect, at 51° it was 1.2%, and at 95° 0.85%. These displacements are also essentially the same as the maximum departures from a smooth curve of any of the other observed points. The results are exhibited in Table VI and Figure 6

TABLE VI.

MAGNESIUM.

Temp °C.	Resistance	Pressure Coefficient			Maximum Deviation from Linearity	Pressure of Maximum Deviation
		At 0 kg.	At 12000 kg.	Average 0–12000		
0°	1.0000	-0.0_5477	-0.0_5311	-0.0_54080	.00238	6500
50	1.1975	462	348	4065	196	5900
100	1.3900	473	341	4018	283	5600

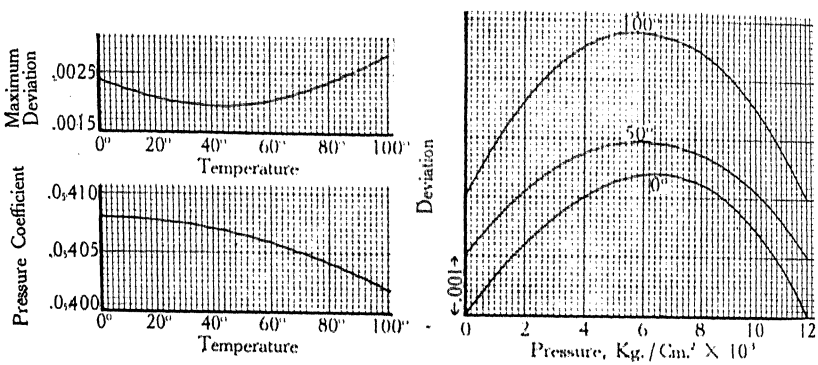


FIGURE 6. Results for the measured resistance of magnesium. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

in the same way as the results of the previous paper. The average pressure coefficient decreased with rising temperature, which is unusual. The relation between resistance and pressure departs from linearity in the usual direction, but it is unusual that the relation is more nearly linear at 50° than at either 0° or 100°. The pressure of maximum departure from linearity moves progressively towards lower values at higher temperatures.

It is interesting to compare these values with those found for the first and presumably less pure sample. The temperature coefficient of the first sample was 0.00412, against 0.00390 for the second, and

the relation between temperature and resistance was linear between 0° and 100°. Here we have the unusual case of the presumably purer substance with a smaller temperature coefficient. Recent observations of Holborn [9] make it likely, however, that the behavior of aluminum is similar, and it is not surprising if the behavior of magnesium and aluminum should be the same. The average pressure coefficients of the first sample between 0 and 12000 kg. were -0.0_5446, 441, and 436 at 0°, 50°, and 100° respectively. This is seen to be about 10% higher than that of the second sample. The two samples agree, however, in having a coefficient which decreases with rising temperature. The maximum departures from linearity of the impurer sample were also nearly the same as for the purer, the maximum deviations being 0.0023, 0.0026, and 0.0029 at the three temperatures respectively. The deviations from linearity of the first sample were symmetrical with respect to pressure, in each case the relation between pressure and resistance being representable by a second degree equation, and the pressure of maximum deviation being at 6000 kg. The first sample differs from the second in not showing a closer approach to linearity at 50° than at the other two temperatures.

These new and more accurate results differ considerably from the rough value given for the first sample; it was stated in the previous paper that the average coefficient for the first sample was probably -0.0_555.

CALCIUM. This material was obtained from the Research Laboratory of the General Electric Co. through the kindness of Dr. Langmuir. An analysis by Mr. N. S. Drake by the method of differences showed not more than 0.1% total impurity, the error of the measurements being 0.1%. Qualitative analysis showed no detectible impurity except a trace of iron, too small to determine quantitatively.

The calcium was furnished in the form of a solid ingot about 1 inch in diameter. Pieces of the appropriate size were cut from it with a hack saw, and were formed into wire 0.013 inches in diameter by extrusion through a steel die. An extrusion pressure of the order of 10000 kg per cm^2 was required. A phenomenon shown to a more or less pronounced degree by all metals during extrusion was particularly prominent with calcium. If the extrusion pressure is pushed too high, or sometimes for no apparent reason, the wire will suddenly break and the metal spit out of the extrusion block in long gulps or small pieces. This spitting forth reaches explosive violence in the case of calcium, and the fine dust into which the issuing wire breaks takes fire spon-

taneously. The explosive sound, the flash of fire and the pungent smoke are likely to be rather terrifying on first experience. For nearly all metals the effect can be greatly reduced by a proper design of the die; the best shape of the die varies from metal to metal.

In spite of the satisfactoriness of the chemical analysis of this sample, it must be recognized that there may perhaps have been in this specimen minute impurities which possibly may have exerted an appreciable effect on the electrical properties. It has been the experience of the General Electric Co. that different samples of calcium, with no perceptible chemical difference, offer very different resistances to extrusion. The effect may not be chemical, and its explanation is entirely obscure. There is no way of knowing whether the specimens difficult of extrusion are more or less likely to be impure, and no connection seems to have been looked for between extrusion and electrical characteristics. The specimen used by me was difficult of extrusion; we cannot now make any use of this fact, but if in the future the cause of the variations should be found, it is well to have the characteristics of this specimen recorded.

Temperature had to be raised to 400° or higher for successful extrusion. Although extrusion would take place at lower temperatures, the wire so formed was brittle, and could be handled only with difficulty. In any event, the best wire that could be formed had to be handled with care. It broke if bent more than once at a sharp angle, and was entirely different in its properties from sodium. Extrusion took place directly into the air, but as the wire exuded from the die, it was wound immediately onto a spool covered with a protecting paste of Nujol and paraffine. Chemical action by the air is much slower than in the case of sodium and lithium, but is no less complete, the wire eventually crumbling away into dust after standing several weeks. Even the Nujol and paraffine does not act as a complete protection, but there is either direct action or else slow diffusion of the air through the protective coating. In order to avoid error from this effect, the wire must be mounted in the pressure apparatus and measurements made as soon after extrusion as possible, while it is still bright. Unless this procedure is followed effects from the high resistance of the surface film are much more troublesome than for any other metal I have tried, not excepting magnesium. With fresh wire, however, such effects become vanishingly small with proper manipulation. The contact resistance may always jump spasmodically under increases of pressure, but with fresh wire the contact can always be sufficiently restored by the momentary passage of a current from a small magneto.

The wire was wound as usual bare on a bone core, and connections made with spring clips, using a protective coating of gold foil at the point of contact.

Runs were made on two samples and at five temperatures, 0°, 25°, 50°, 75° and 96°. The runs on the first sample were terminated by the failure of the insulation of the three-terminal plug. The transmitting medium was Nujol and petroleum ether. Chemical action was never entirely absent, but as in the case of sodium, it was mostly confined to low pressures. It increases rapidly with rising temperature, and at 96° was so rapid that 1500 kg. was the lowest pressure at which readings were attempted. Unlike sodium and lithium, calcium shows pronounced seasoning effects of pressure, and the runs at 25° and 75°, which were those of the initial application of pressure to the two samples respectively, were much less regular than the subsequent runs. Because of the necessity of obtaining readings rapidly because of chemical action, preliminary seasoning applications of pressure were omitted, and the initial runs were included in the final results. At 25° the total zero shift (initial application) was 1.2% of the total pressure effect; at 0° 0.5%; at 50° 3.9%; at 75° (initial application) 6.9%; and at 96° (zero taken from 1500 kg.) 3.3%. At 25° and 75° the individual points lie very closely on two smooth curves, different for increasing and decreasing pressure. The incomplete seasoning shows itself in a sequence of readings like that of an open hysteresis loop. The open end of this loop at atmospheric pressure has the width given above by the zero displacements. At the other temperatures the readings also show a tendency to hysteresis effects, but the departure from the mean is much less. At 0° the maximum departure of any single point from the smooth curve representing the mean of the points with increasing and decreasing pressure is 1.2% of the total effect; at 50°, 1.5%; and at 96°, 1.5%.

The temperature coefficient of resistance at atmospheric pressure was determined by the same method and at the same time as the readings for sodium and lithium. The "observed" resistances, which are the mean of points with ascending and descending temperature, at four temperatures (0°, 25°, 50°, and 75°) all lie within the limits of error (one part in 7000) on a second degree curve. The total shift of the zero during the run, presumably due to chemical action, was 1.6% of the total temperature effect. The value given in the table for the resistance at 100° was obtained from the second degree curve by extrapolation. The mean coefficient between 0° and 100° determined in this way is 0.003327.

The temperature coefficient of resistance of Calcium at atmospheric pressure has been previously measured by Northrup,[11] who found between 0° and 100° the value 0.00246, and by Swisher,[10] who found the relation between temperature and resistance to be linear between 0° and 600°, and the coefficient to be 0.00364 of the value at 0°. An examination of Swisher's results shows that there were considerable irregularities, and that within his limits of error it is not possible to say whether his coefficient between 0° and 100° is greater or less than my value above. The low value of Northrup is probably due to impurity in his sample.

In smoothing the experimental results for the most probable final values, the usual procedure was followed. The results at each temperature were first smoothed independently, and then readjusted so as to give smooth temperature differences. The effect of insufficient seasoning in the runs at 25° and 75° was shown by the greater readjustments necessary at these temperatures. The maximum readjustment necessary was 0.0% at 0°, 1.6% at 25°, 1.4% at 50°, 1.8% at 75°, and 0.4% at 96°.

TABLE VII.

CALCIUM.

Pressure kg/cm²	Resistance 0°	25°	50°	75°	100°
0	1.0000	1.0748	1.1552	1.2402	1.3327
1000	1.0107	1.0859	1.1668	1.2522	1.3454
2000	1.0217	1.0974	1.1789	1.2651	1.3589
3000	1.0330	1.1092	1.1912	1.2780	1.3725
4000	1.0447	1.1213	1.2039	1.2914	1.3865
5000	1.0569	1.1340	1.2171	1.3051	1.4008
6000	1.0696	1.1473	1.2309	1.3193	1.4157
7000	1.0827	1.1609	1.2451	1.3341	1.4311
8000	1.0963	1.1751	1.2599	1.3495	1.4470
9000	1.1103	1.1896	1.2749	1.3650	1.4631
10000	1.1247	1.2045	1.2903	1.3810	1.4797
11000	1.1396	1.2200	1.3064	1.3976	1.4969
12000	1.1550	1.2360	1.3229	1.4147	1.5146
Average Coefficient 0–12000 kg.	$+0.0_41292$	$+0.0_41242$	$+0.0_41210$	$+0.0_41172$	$+0.0_41137$

The final results for resistance as a function of pressure and temperature are given in Table VII. The striking and unexpected result, as in the case of lithium, is the positive coefficient. The coefficient is greatest at the lowest temperature, having the average value $+0.0_41292$ at 0°. Both the instantaneous and the average coefficient increase with rising pressure. In both these particulars the behavior is much like that of bismuth. The absolute value of the coefficient is of the order of half that of bismuth.

Bismuth is abnormal in so many other respects than its pressure coefficient, that it seemed of interest to find whether calcium has the same sort of abnormalities. The large increase of resistance of bismuth in a magnetic field is one of the well known abnormal effects. I tried the effect of a field of approximately 27000 Gauss on the resistance of a coil of calcium, the wires of the coil being everywhere at right angles to the field, and found a decrease of resistance of only 1 : 1600. It is evident, therefore, that any parallelism between the conduction mechanisms of calcium and bismuth cannot be very complete. A more exhaustive investigation of the various properties of calcium than has yet been made seems well worth while.

In a previous paper it has been shown that the abnormal positive pressure coefficients of resistance of bismuth and antimony are associated with values of the thermal expansion abnormal as compared with the other properties. The same comparison for calcium appeared of interest, but the thermal expansion of calcium has apparently not been previously measured, and I accordingly made special measurements of it.

The thermal expansion was determined by ordinary methods, using a glass dilatometer. The calcium was the same specimen as that from which the resistance sample was cut. It was turned over its entire surface in the lathe, and finished to a cylinder about 6 cm. long and 20 cm^3 volume. The surface was smooth, without blowholes. In the glass dilatometer the calcium was surrounded with Nujol. The calcium and Nujol had been previously heated together in another vessel to 100° to avoid as far as possible chemical action during the dilatometer readings. Discoloration of the surface of the calcium by this preliminary heating was very slight. Air bubbles in the dilatometer were avoided by filling in vacuum. The Nujol is so viscous that without special precaution error may be introduced by sticking of the Nujol to the walls of the capillary. This error was avoided by heating the capillary before the readings with a small gas flame, and by making readings with increasing temperature. A pre-

liminary attempt was made to avoid the error by using petroleum ether as the medium, which is very much more fluid than the Nujol. This was unsuccessful because of chemical action between the petroleum ether and the calcium. Readings of the expansion of the calcium and Nujol were made at 0°, 25°, and 50°. At 50° a very few exceedingly minute bubbles appeared, probably the beginning of chemical action. Accordingly the readings at 50° were discarded. The auxiliary data needed in the computation were obtained from the dilatations when the dilatometer was entirely filled with Nujol and with mercury respectively. The volumes of the dilatometer and the capillary were obtained by weighing the mercury required to fill them. The bore of the capillary was calibrated for uniformity by conventional methods. The density of the calcium was obtained by weighing it in air and under Nujol. The densities given are corrected for vacuum.

The following values were obtained for calcium:

Density at 21° 1.5563
Coefficient of volume expansion, 0° to 21°, 0.000075.

The values for Nujol were obtained incidentally and are recorded.

Density at 21° 0.8786
Coefficient of volume expansion, 0° to 21°, 0.000717.

Strontium. Particular interest attaches to this metal because of the fact that it is underneath calcium in the periodic table, and calcium is unusual in having a positive coefficient. The material I owe to Dr. G. E. Glascock, who very kindly placed at my disposal some of the material whose preparation and properties he has described.[12] The metal was prepared by the electrolysis of the fused salts. It was in the form of fused nodules of sometimes two or three cubic centimeters volume, and had been kept since preparation under kerosene. Some sort of action had taken place between the metal and the kerosene, under which most of the kerosene disappeared, and the metal became coated with a fine gray powder. The action of calcium on kerosene I have found to be very similar. On scraping off the gray powder, the coherent metal is found underneath. On cutting into the cleaned nodules with a cold chisel, slag-like inclusions are sometimes found. Lithium prepared by electrolysis shows the same appearance. By careful selection it was possible to find pieces large enough free from these inclusions.

The measurements were made on the metal in the form of wire approximately 0.020 inches in diameter, formed by extrusion from one

of the selected pieces of clear metal. The extrusion is considerably easier than that of calcium, and may be successfully performed at a temperature of 230°. At room temperature the metal spits out of the die in small pieces. The wire is fairly soft and pliable and can be bent to a radius of perhaps ten times the diameter of the wire, but it is quite different in mechanical properties from the alkali metals, such as sodium, and shows brittleness if too sharp a bend is attempted.

Previous measurements on the electrical properties of strontium seem to have been published only by Matthiesen.[8] He extruded the metal to wire in much the same way as above. He gives for the specific resistance at 20° the value 25×10^{-6} ohms per cm. cube. I found at 0° for my specimen the value 30.7×10^{-6}. This specimen is presumably considerably purer than Matthiesen's, and this value would seem to be preferred. Matthiesen did not attempt to measure the temperature coefficient of resistance, probably because of resistance of the contacts. He did not use a potentiometer method, but had to correct as best he could for the resistance of his leads and contacts. With a potentiometer method as used here, there is no such difficulty. There is difficulty, however, in the chemical action accompanying changes of temperature, which produces permanent changes of resistance. Error from this effect was avoided by the same procedure as that used previously for the alkali metals. Four thermostated baths were kept simultaneously in operation, and the specimen transferred rapidly from one to another. The bare wire was immersed in a glass tube of Nujol for the measurements, the Nujol having been previously heated with sodium to remove all moisture and exhaust as far as possible all tendency to chemical action. There nevertheless seems to have been some specific action between the oil and the strontium. About fifteen minutes were required for the attainment of temperature equilibrium after the wire had been transferred from one bath to the next. Readings were made with ascending and descending temperature between 0° and 96°, starting with 0° and ending with 0°. The mean of the ascending and descending readings was taken as the true effect. The permanent change of zero after the excursion was 12% of the maximum effect. The mean coefficient between 0° and 100° found from these readings was 0.00384. The effect is not quite linear with temperature, but the change becomes more rapid at the higher temperatures, as is normal.

The value of the temperature coefficient is quite normal for pure metals, and in the absence of further information, makes it probable that this material was of satisfactory purity. It is not possible to

obtain the analysis from the paper of Glascock, because the products of his separate electrolyses were not always of the same purity, and the different batches were indiscriminately mixed in the material as supplied to me. The least pure of any of the specimens of Glascock had about 2% impurity, and the best about 0.15%.

Pressure measurements were made in the regular way with the potentiometer. The wire was used bare, and the connections were made with spring clips. The resistance of the contacts increased during the runs, and sometimes became troublesomely large; it could then be reduced by passing a high tension current from a small magneto through the contacts. The wire was seasoned by a preliminary application of 3000 kg. at room temperature; there was no perceptible change of zero after this application. Three runs were made; at 0°, 50.5°, and 97°. At the highest temperature the zero of pressure was taken as 500 kg. in order to prevent chemical action, and the value at atmospheric pressure obtained by extrapolation. Considering the chemical activity of this material the readings showed a gratifying regularity. At 0° there was a permanent change of zero of 1.8% of the total effect, at 50° the change was 0.3%, and at 97° 2.1%. The maximum departure of any of the other points from the smooth curve was 1.6% at 0°, 1.2% at 50°, and except for one bad point, 1.5% at 97°. The observed resistances were smoothed and a table constructed for the resistance at regular intervals of pressure and temperature in the regular way.

The results are shown in Table VIII and Figure 7. The resistance increases under pressure, the same as for calcium. The increase is furthermore very large; it is five times as large as that of calcium, and three times that of bismuth, and is the largest positive coefficient yet found. The behavior is in other respects like that of other metals with a positive coefficient. When the resistance is plotted against pressure, the curve is concave upwards, the change becoming more rapid at the higher pressures. The coefficient becomes markedly smaller at the higher temperatures. The instantaneous coefficient becomes smaller at the higher pressures; this was not the case for bismuth. One may be puzzled at first by the Table which shows a smaller instantaneous coefficient at both 0 kg. and 12000 kg. than the average coefficient between 0 and 12000. The reason for this is that the instantaneous coefficient is calculated in terms of the resistance at the pressure in question, which becomes rapidly greater at the higher pressures, whereas the average coefficient is calculated in terms of the initial resistance at 0 kg. The resistance shows a regular drift

TABLE VIII.

STRONTIUM.

Pressure kg/cm²	Resistance 0°	50°	100°
0	1.0000	1.1768	1.3828
1000	1.0516	1.2320	1.4341
2000	1.1058	1.2906	1.4908
3000	1.1622	1.3519	1.5539
4000	1.2220	1.4166	1.6214
5000	1.2850	1.4842	1.6936
6000	1.3508	1.5544	1.7712
7000	1.4196	1.6280	1.8527
8000	1.4916	1.7051	1.9381
9000	1.5670	1.7852	2.0272
10000	1.6462	1.8684	2.1198
11000	1.7290	1.9550	2.2157
12000	1.8160	2.0446	2.3144
Average Coefficient 0–12000 kg.	$+0.0_46800$	$+0.0_46146$	$+0.0_45611$
Coefficient at 0 kg.	0.0_4502	0.0_4456	0.0_4351
Coefficient at 12000 kg.	0.0_4492	0.0_4451	0.0_4432

with increasing temperature. At 0° the third derivative of the resistance as a function of pressure is positive, at 50° it is zero, and at 100° it is negative.

MERCURY. I have already published results for the resistance of liquid mercury as a function of pressure and temperature,[13] but I have now found it possible to considerably extend the range of the previous work. Previous work on the liquid was between 0° and 50° and to 6500 kg., and a few very rough qualitative results were obtained for the solid. The results for the liquid have now been extended over the temperature range 0° to 100° and over the pressure range to 12000 kg. In addition, the resistance of the solid has been accurately meas-

ured at 0° between the solidifying pressure (7640) and 12000 kg., and the change of resistance on solidifying at 0° has been also determined.

The liquid was measured with the Carey Foster bridge, by the same method used for most metals in the form of fine wire. The mercury was contained in a U-shaped capillary, and connections were made to

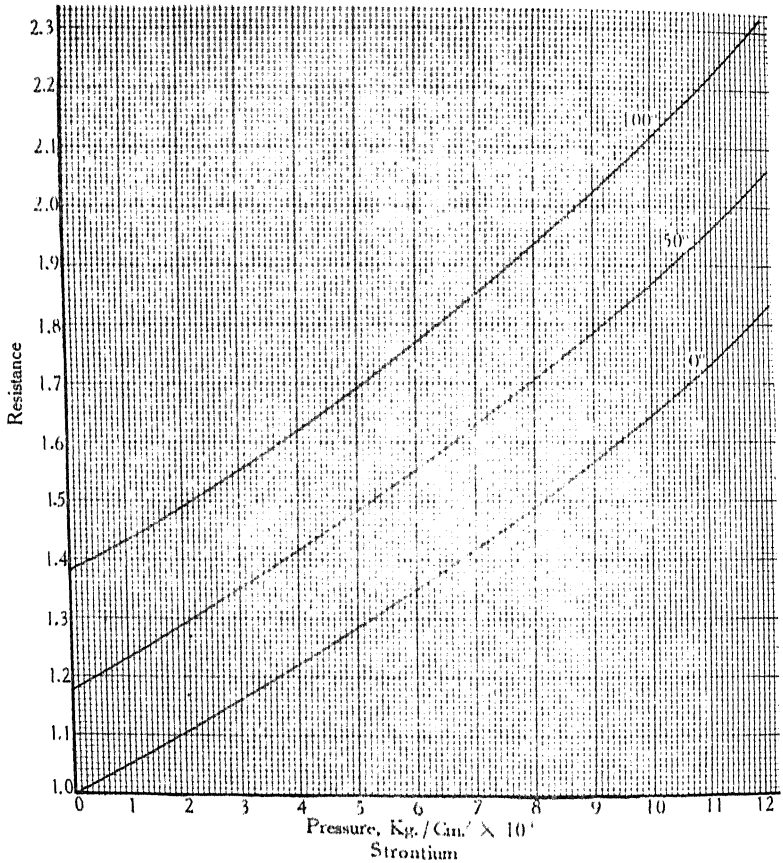


FIGURE 7. Relative resistances of strontium at several constant temperatures as a function of pressure.

the mercury by amalgamated copper wires dipping into cups at the upper ends of the U. The resistance was about 10 ohms. The capillary was of Jena glass No. 3880a, the same grade of glass as that used in the previous work. This particular capillary was blown in 1907,

and had been last used in 1911, when it had been exposed to the freezing pressure of mercury at 0°, and had since been resting in a dust proof container. The measurements on the liquid recorded here were made in 1917. The technique of the previous work has been considerably improved in the interval between 1908 and 1917. The transmitting liquid used in 1908 was a mixture of water and glycerine, and elaborate precautions had to be taken to avoid short circuits. The liquid is now a hydrocarbon, and the insulation properties are perfect. The values now obtained for the change of resistance differ by about 1.5% from the previous ones. Part of this difference is perhaps to be ascribed to improvement in technique, part to change in the behavior of the glass, which has been resting ten years since blowing and annealing, and perhaps part to difference in the standard of pressure. My very earliest results, which reached to only 6500 kg., depended on a pressure gauge of smaller range and somewhat different construction from that used in all my subsequent work reaching to 12000 kg. or more. All this later work depends on the same gauge, and assumes as the fundamental constant that the freezing pressure of mercury at 0° is 7640 kg. Any discrepancy now found with the former values for the resistance of mercury cannot affect the validity of any of the later work up to a range of 12000 kg.

The glass was seasoned before the measurements by an application of 11300 kg. at room temperature, and then by raising temperature to 96° while still under pressure. Five runs were made on the liquid, in addition to the seasoning runs; these were at 0°, 26°, 50°, 76°, and 97°. The maximum zero displacement after a run at any of the temperatures was 0.46% of the total effect. The maximum departure from a smooth curve of any of the observed points at any temperature was 0.6% of the total effect, and the points usually lay on a smooth curve within the sensitiveness of the readings, which was about one part in 5000 of the maximum effect.

The observed results were smoothed for pressure and temperature and a table constructed for the resistance at uniform intervals of pressure and temperature in the regular way. The resistance of the liquid is shown in Table IX, and the coefficients are shown later in Table XX. The resistances given in this table are corrected for the compressibility and thermal expansion of the glass, using the values already given. The correction for temperature amounts to a change of observed resistance of 0.0007 for the range of 100°, which is about 0.74% of the measured effect, and the correction on the pressure effect is 0.0007 for 1000 kg., which is initially 2.2% of the pressure change. The values given in the Table are, therefore, relative values of the

TABLE IX.

RELATIVE SPECIFIC RESISTANCE OF LIQUID MERCURY.

Pressure kg/cm²	Resistance 0°	25°	50°	75°	100°
0	1.0000	1.0240	1.0480	1.0719	1.0959
1000	.9689	.9911	1.0137	1.0360	1.0574
2000	.9400	.9609	.9823	1.0032	1.0224
3000	.9136	.9331	.9533	.9726	.9902
4000	.8894	.9076	.9268	.9449	.9611
5000	.8667	.8838	.9023	.9192	.9345
6000	.8459	.8615	.8793	.8951	.9096
7000	.8263	.8408	.8579	.8729	.8866
8000		.8214	.8377	.8516	.8650
9000		.8034	.8200	.8318	.8445
10000		.7863	.8010	.8133	.8254
11000		.7704	.7841	.7958	.8071
12000		.7554	.7684	.7790	.7895

specific resistance, that is, they are the relative values of the resistance which would be shown by a body of mercury of invariable dimensions, but with the total mass changing with pressure and temperature.

Certain differences between the new and the old results should be mentioned. At 25° the change of resistance under 6500 kg. is now found to be 0.1586, against the old value 0.1562. The previous formula given for the resistance up to 6500 kg. gives rather good results when used for extrapolation to 12000 kg. At 25° the observed decrement of resistance is now found to be 0.2622 against the value 0.2600 computed by the formula previously given. The difference is approximately the same as that between the previous and the present observed values at 6500 kg. Over the narrower temperature range of the previous work the effect of temperature was taken as linear at any constant pressure. Over the greater temperature range of the present work, this is found not to hold, but the effect of temperature becomes greater at the higher temperatures, and passes through a minimum near 25°. At atmospheric pressure, however, the relation between resistance and temperature is still found to be linear within the limits of error, which are about 5/10,000 of the total resistance.

The resistance of the solid under pressure was measured by filling

a capillary of very thin glass with the liquid, exposing to a pressure sufficient to freeze it, and making measurements on the solid contained in the glass without allowing the pressure to fall low enough to melt the mercury. By the use of thin glass I hoped to eliminate error due to the constraining action of the container. It was necessary to use a capillary of rather large section, because of the mechanical difficulties of blowing and handling a very fine capillary with excessively thin walls, and the potentiometer method of measurement was therefore used. The leads were of fine platinum sealed through the glass. Under pressure the glass cracked around the seals, but of course this introduced no error in the measurements of the solid. Only one set of measurements was made on the resistance of the solid, at 0°. Measurements were made on the liquid up to the freezing pressure, pressure was then increased very cautiously beyond the freezing point so that freezing took place slowly, and the solid so formed was seasoned by an excursion to 12000 kg. and back nearly to the freezing pressure. Readings were now made in the domain of the solid to 12000 kg. These readings were exceedingly regular; they showed no departure from the smooth curve within the sensitiveness of measurement, which amounted to one part in 1500 on the total effect for the range 7640 to 12000 kg. This was gratifying, because it showed that the very thin glass exerted no perceptible constraining effect. In the previous work with the liquid in heavy glass capillaries very irregular results were found after the metal had frozen.

The relative values for the resistance of the solid are shown in Table X in terms of the resistance of the solid at 7640 kg. and 0° as unity. In comparing these values with those of the liquid it must be remembered that the values for the solid are relative values of the "observed" resistance, and must be corrected by a factor equal to the linear compressibility in order to give relative values of specific resistance. The pressure coefficient of "observed" resistance may be found from the table to be -0.0_4236, and within the sensitiveness of the measurements it is constant over the pressure range from 7640 to 12000. This value for the pressure coefficient is somewhat higher than the minimum value set in the previous work, which was -0.0_42. The accuracy of the previous work for the solid was so low that it was stated that the maximum value for the solid might not impossibly be ten times the minimum. The pressure coefficient of the solid is very nearly that of the liquid, which is -0.0_4224 at 6500 kg., when corrected by one third the volume compressibility of the liquid mercury so as to be strictly comparable with the value for the solid. It is surprising

TABLE X.

Relative Specific Resistances of Solid Mercury at 0° C.

Pressure kg./cm.	Resistance
7640	1.00000
8000	0.99185
9000	0.96870
10000	0.94615
11000	0.92405
12000	0.90250

The ratio of the resistance of the liquid to that of the solid at the freezing point at 0° and 7640 kg. is 3.345.

that the values for the solid and the liquid are so close, and still more surprising that the value for the solid is greater than that for the liquid. The former rough work suggested the opposite and more natural behavior.

The ratio of the resistance of the solid to that of the liquid at the freezing pressure may also be calculated from the measurements. In view of the extreme care taken to compel the freezing to go slowly, and the fact that when the apparatus was taken apart the capillary was found cracked only at the bend, it is probable that the observed ratio of resistance of solid to liquid refers to the relative resistances of material occupying space of the same dimensions in the liquid and solid states, that is, to relative values of the specific resistance. The value found for the ratio of resistance of liquid to solid at 0° and 7640 kg. (the equilibrium coördinates) was 3.345. This falls within the range of the very irregular values found in the previous work.

GALLIUM. The raw material from which this rare metal was prepared I owe to the kindness of Dr. K. Stock of the Bartlesville Zinc Co. The purification I owe to the kindness of Professor T. W. Richards. He was engaged in a redetermination of the atomic weight and certain other physical properties, and was kind enough to include some of my raw material with his, and let me have some of the purified product.

The actual work of purification was done by Mr. [illegible] direction of Professor Richards. The final product [illegible] 0.01% total impurity. Professor F. A. Saunders [illegible] make a spectroscopic analysis for me, and was able [illegible] of zinc as the impurity. There may also have been [illegible] present.

There was available for my measurements about one [illegible] was ample for a determination of the effect of pressure [illegible] and also for a determination of the variation of freezing [illegible] with pressure and an exploration for other allotropic [illegible] (which had not been previously done) but was [illegible] determination of the change of volume on freezing [illegible] freezing data are, therefore, not yet determined.

The measurements here described include the [illegible] the liquid, temperature coefficient of resistance of [illegible] at atmospheric pressure, change of resistance with [illegible] to the liquid, effect of pressure on resistance of [illegible] and variation of freezing pressure with temperature.

The determination of the freezing curve and the [illegible] new modifications was the first task, in order to [illegible] which the resistance measurements were to be conducted. [illegible] is, of course, abnormal in that it expands when it freezes, and the freezing temperature is accordingly depressed under increased pressure. It would not be unnatural to expect new modifications at high pressures like the other modifications of ice. Because of the limited quantity of material available the method of exploration for new modifications had to be an electrical one. It was my original intention to form the material into wire by extrusion, and to measure the resistance of the solid as a function of pressure at different temperatures. A change from one modification to another would be known by a discontinuous change of resistance, and melting be open to sounding. Unexpected difficulties were found in the extrusion. If the extrusion is performed at room temperature, the metal melts under the one-sided stress instead of extruding (the melting temperature is 29.85°), and if this effect is avoided by lowering the temperature, the metal becomes so exceedingly stiff and brittle that extrusion is very difficult. After an unsuccessful attempt at room temperature, I tried extrusion at the temperature of ice and salt. At this temperature the metal spit out of the die in short pieces. However, by careful work, I did get a few inches of wire at this extrusion temperature. Perhaps some intermediate temperature would be more successful

Mechanically the extruded wire is very crystalline and brittle, and will support almost no bending. When enclosed in a glass capillary, however, and if the capillary breaks across without breaking the gallium, as sometimes happens when the capillary is ruptured by freezing, the metal may be pulled out by a tensile stress and appears as ductile as lead.

The extruded wire was used in an attempt to find the melting curve. Short lengths were layed horizontally between two copper wires, short-circuiting them. It was expected that when melting took place the system would open circuit. The surface tension of the gallium proved to be so high, however, that this method did not work. The metal, even when melted, only sagged between the supports, and no measurements could be made. Several modifications of this scheme were tried with indifferent success. These preliminary measurements made pretty evident, however, that there were no new modifications, and that above the normal melting point the metal remains liquid at all pressures below 12000 kg.

Measurements were now made on the resistance of the liquid as a function of pressure above the melting temperature. The liquid gallium was enclosed in a glass capillary, provided with four platinum terminals, and measurements made by the potentiometer method. The capillary was filled in high vacuum to avoid error from air sticking to the walls. From a comparison of the resistance of the capillary when filled with gallium and when filled with mercury it was possible to obtain the resistance of gallium in terms of that of mercury, and so the specific resistance of liquid gallium.

After completion of measurements on the liquid, the temperature of the apparatus was lowered into the region of the solid, and after some trouble, the liquid was induced to freeze. The melting curve was now determined by finding, as a function of temperature, the pressure at which the resistance began to change discontinuously. It was necessary to do this very cautiously. In changing pressure the thermal effects of compression might easily be sufficient to entirely melt the gallium, when long and tedious manipulation would be necessary to make it freeze again, because of the well known property of supporting great subcooling. In this way the melting curve was mapped out to 12000 kg.

Measurements were also made on the resistance of the solid as a function of pressure while enclosed in the glass envelope, but there were irregularities, and it was evident that the solid must be unconstrained in order to give reliable results. Accordingly a small rod

of solid gallium was sculptured out with considerable difficulty with a warm wire as a sculptor's tool, four platinum terminals were set into it, and measurements made of the pressure coefficient of resistance by the potentiometer method. The temperature coefficient of the solid at atmospheric pressure was also determined with this free specimen. This seems to be the first time that this has been done. Previous measurements of the temperature coefficient of the solid have been on the solid in glass, and no correction has been applied for the constraining effect of the glass. After the completion of the resistance measurements on the free solid another point was found on the melting curve, which checked with the points found previously. The resistance of the solid showed no discontinuities within the errors of the measurements, and hence it is not likely that there are new modifications in the region of the measurements. This was rather a disappointment.

TABLE XI.

GALLIUM.

Melting Curve.

Pressure kg/cm²	Temperature °C.
0	29.85°
1000	27.8
2000	25.7
3000	23.55
4000	21.4
5000	19.2
6000	17.0
7000	14.8
8000	12.6
9000	10.35
10000	8.10
11000	5.85
12000	3.55

The smoothed coördinates of the melting curve are given in Table XI, and the observed points with the curve are shown in Figure 8. For the melting point at atmospheric pressure I used the value determined for this sample by Mr. Boyer, which is 29.85°. This is lower than the value originally given by deBoisbaudran,[14] 30.15°,

but is higher than that given by Guntz and Broniewski,[15] 29°. The value of Boyer is the mean of a number of values determined with extreme care, and is seen to fit perfectly with the values which I have found at higher pressures. Considering the extreme purity of this sample, there is every reason to give this value the preference.

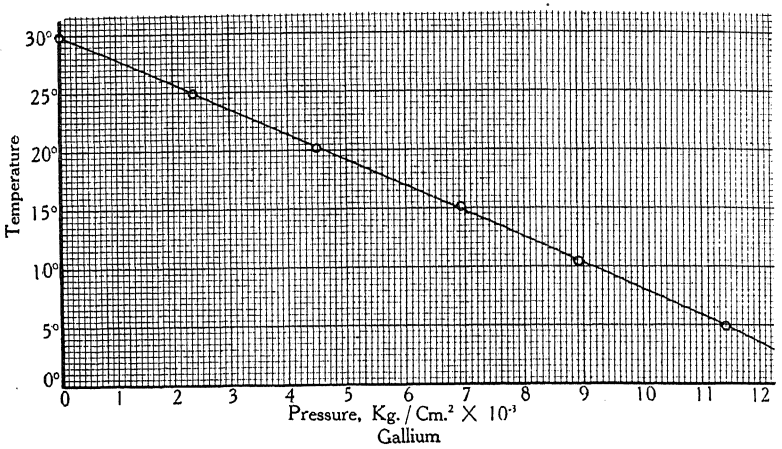


FIGURE 8. The melting curve of gallium.

The melting curve has the same form as that of water and bismuth, the only other substances I know with curves of this abnormal type. It is characteristic of these curves that the slope becomes numerically greater at the higher pressures. The slope of the melting curve of gallium increases numerically by about 15% in the pressure range of 12000 kg.

The slope of the melting curve may be combined with other data to give the latent heat on melting. Boyer's values for the densities of the solid and liquid at the melting point are 5.90 and 6.09 respectively. This gives 0.00529 for the change of volume per gm. on melting. Taking from the above curve the value 0.00203 for the initial slope of the melting curve, and substituting in Clapeyron's equation, we find 18.5 cal. per gm. as the latent heat of melting. Boyer has recently determined this to be 19.1. The agreement is probably within the error of the density determinations. The variation of the latent heat along the melting curve cannot be found until the variation of the change of volume along the melting curve is also known, and this will require a larger sample.

The ratio of the resistance of the liquid to that of an equal volume

of mercury at the melting point was found to be 0.2683, against the value, 0.272 of Guntz and Broniewski.[14] Taking for the specific resistance of mercury at this temperature 96.59×10^{-6}, this gives 25.92×10^{-6} for the specific resistance of liquid gallium at the melting point.

Three runs were made on the resistance of the liquid as a function of pressure, at 34.2°, 62.5°, and 94.4°. Before the final measurements another run was made on another sample. This run had somewhat greater error, but agreed with the final results within the irregularities of the measurements. The resistance measurements of the liquid showed a distinct hysteresis, doubtless due to the action of the glass capillary. Any such effects would be expected to be especially large for gallium because the pressure coefficient of resistance is so low. The difference between readings with increasing and decreasing pressure might amount to 2.5% of the maximum effect. Except for this, the points lay regularly within the sensitiveness of the readings. The values obtained from these three runs were smoothed in the regular way, and the resistance tabulated at regular intervals of temperature and pressure. The results are shown in Table XII. In this table

TABLE XII.

GALLIUM.

Relative Specific Resistances of the Liquid.

Pressure kg/cm²	Resistance 30°	65°	100°
0	0.6456	0.6647	0.6824
1000	.6415	.6605	.6783
2000	.6380	.6564	.6743
3000	.6342	.6527	.6705
4000	.6308	.6488	.6667
5000	.6272	.6452	.6629
6000	.6238	.6418	.6593
7000	.6205	.6383	.6558
8000	.6171	.6349	.6522
9000	.6139	.6316	.6486
10000	.6105	.6283	.6451
11000	.6075	.6252	.6418
12000	.6044	.6223	.6386
Average Coefficient 0–12000	-0.0_5531	-0.0_5532	-0.0_5534

the unit of resistance is the resistance of the solid at atmospheric pressure and 0° C. There may be some question as to the accuracy of the value for the ratio of resistance of solid to liquid, but this cannot affect the relative accuracy of the values listed in the table for the resistance of the liquid.

The values listed in the table have been corrected for the thermal expansion and compressibility of the glass, so that the values are proportional to the specific resistances. In making this correction the thermal expansion of the glass was assumed to be 0.0_58, and the linear compressibility 0.0_67. The correction for thermal expansion is small, and any error in the value assumed for the coefficient cannot appreciably affect the results, but because of the smallness of the pressure coefficient of resistance, the correction for the compressibility of the glass is rather important. The correction for compressibility, as given in the table, amounts initially to 11% of the pressure coefficient. The compressibility of different varieties of glass varies a good deal; it is perhaps conceivable that the value assumed is as much as 20% different from the correct one, so that the possibility must be recognized that the values given in the table for the pressure coefficient of resistance may be in error by as much as 2%. However, any correction of this sort will not affect the relative curvature, since the compressibility of glass is sensibly linear, and it seems justified to retain all the significant figures of the table. The effect of the corrections for the glass is to increase both the observed temperature and pressure coefficients of resistance.

The average pressure coefficient of the liquid to 12000 kg. is seen to vary little with temperature. In absolute value it is somewhat less than one half that for bismuth, and one sixth that for liquid mercury. The curvature is in the normal direction, that is, the coefficient becomes less at the higher pressures.

The pressure coefficient of resistance of the solid was measured only at 0°; at this temperature the entire pressure range of 12000 kg. was available, whereas at higher temperatures the pressure range was restricted by the melting, and the accuracy was proportionally less. The absolute resistance of the specimen was low, so that measurements could not be made with as much accuracy as usual. Beside the final run from which the tabulated results were taken, several rougher runs were made with other samples; these agreed with the final results within the accuracy of the measurements. Within the limits of error the relation between resistance and pressure is linear at 0° to 12000 kg., and the coefficient is -0.0_5247. The maximum departure of

any of the observed points from a linear relation was 2.7% of the total effect.

The constraining effect of a glass capillary on the solid is shown by the low value, -0.0_5191, found for the coefficient of the solid in glass.

The pressure coefficient of the solid is seen to be negative, that is, normal. This was rather a surprise; I had anticipated because of the abnormal expansion on freezing and the fact that bismuth also expands on freezing and has a positive coefficient of resistance that the coefficient of gallium might be positive also. The numerical value of the coefficient of the solid is quite normal, when compared with other metals. It is the value characteristic of a hard metal, which in most other cases also means a metal with a high melting point. The coefficient of the solid is of the order of one half that of the liquid. This again is as one would expect, except for the abnormal volume relations on freezing. However, the solid is less compressible than the liquid in spite of its greater volume [15a]; so that from this point of view the relative magnitudes of the pressure coefficients of liquid and solid do not seem unnatural.

The temperature coefficient of resistance of the unconstrained solid was obtained from readings at 0° and 21.5°. The value for this range is 0.003963, an entirely normal value. Previous values for this coefficient are exceedingly uncertain. Guntz and Broniewski's readings were quite irregular, the effect even reversing in sign above 18.6°. This may have been due to the constraining effect of the glass; such an effect is to be expected, and in the observed direction.

It may be mentioned that I made measurements on the subcooled liquid at 0°, and found the resistance to lie on a regular prolongation of the curve for the resistance above the melting point. Guntz and Broniewski, on the other hand, found the resistance of the liquid to pass through a minimum and to increase again in the unstable region below the melting point.

The ratio of the resistance of the solid to that of the liquid at the freezing point was found from measurements of the resistance of the solid at 0° in the glass capillary and the resistance of the liquid in the same capillary. The resistance of the solid was extrapolated to the melting point with the coefficient found. This procedure may be open to some question, but it seemed as satisfactory as any other that presented itself. The specific resistance of the solid was found to be 1.733 times that of the liquid at the melting point. Notice that the relative magnitude of the volumes governs the relative magnitudes of the resistance; the solid with the larger volume also having the larger

resistance. Güntz and Broniewski found 2.09 for the ratio of the two resistances.

TITANIUM. By the kindness of the Research Laboratory of the General Electric Co. I was enabled to make measurements on a filament of titanium deposited on tungsten, which had been used for experimental work with incandescent lamps. The dimensions of the tungsten core were such that the total impurity of tungsten was only 1.8%. The method of deposition of the titanium on the core is not known to me; the surface of the filament was distinctly crystalline in appearance, probably due to recrystallization after deposition. It had been glowed out in vacuum at high temperature after deposition in order to remove impurities of hydrides, nitrides, and oxides, all of which are readily formed with this substance. This glowing out must have produced alloying with the tungsten core, and the alloy so formed is evidently quite different in its properties from the pure metal. This may be stated with confidence because the General Electric Co. found for the specific resistance of this filament the value 350×10^{-6} ohms per cm. cube, which is higher than would be given by the tungsten core alone. The same thing is indicated by the low value of the temperature coefficient, which was 0.000221.

The difficulties of the pressure measurements were very great, and it was not possible to obtain results which were at all regular. It can be stated only that the pressure coefficient is exceedingly small, probably not greater than 10^{-7} per kg., and that the likelihood is that the resistance increases with pressure.

ZIRCONIUM. Two filaments deposited on tungsten in the same way as the titanium were made available through the kindness of the General Electric Co. The treatment of the filaments had been the same as that of titanium. It is probable that the temperature of glowing out had been sufficient to produce alloying with the tungsten core. This is strongly suggested by the low value for the temperature coefficient of resistance, which, between 0° and 100°, was 0.00004 for one specimen, and 0.00058 for the other. The dimensions of the wires on which these filaments were deposited would indicate a total impurity of tungsten of 1.8% and 0.6% for the two samples respectively. The impurer sample has the smaller coefficient, as is usual. The exceedingly low value of both coefficients indicates that the impurity has a specific effect, and that any results found for the pressure coefficient may not be very close to the values for the pure metal.

In view of the probably large effect of the impurity, and also of the difficulty of the measurements, a great deal of effort was not

put on this substance. The potentiometer method of measurement was used. This substance cannot be soldered, so that it was necessary to make connections with fine springs; slipping of the springs was perhaps accountable for some of the irregularities. The surface layer has a very high resistance, which again introduced irregularities at the spring contacts.

Two runs were made on the impurer specimen, at 0° and 94°. The irregularities of the second run were so great that the results were not computed. Within the limits of error the relation between pressure and resistance is linear at 0°, and the coefficient is -0.0_65.

The results on the second and purer sample were much more regular. Readings were made at 0° and 95°. At both these temperatures the relation is linear to 12000 kg. The best value for the pressure coefficient is -0.0_6398 at 0°, and -0.0_6396 at 95°. The coefficient is seen to be very small; such small values have been found only for certain of the high resistance alloys. The specific resistance of these Zirconium filaments was also very high; 200×10^{-6} ohms/cm^3 is the value given me by the General Electric Co.

Arsenic. Considerable interest attaches to this element because of its position in the periodic table above bismuth and antimony and below black phosphorus, all of which are abnormal in behavior under pressure. The arsenic used in this experiment was furnished by Eimer and Amend. It had been distilled in vacuum, but was otherwise of ordinary commercial quality, and I have no way of knowing what the impurities might have been. I attempted to cast it in a mold of pyrex glass, supported on the outside with magnesia, and enclosed in an iron pipe with caps tightly screwed on the ends. The melting temperature of arsenic was high enough to melt the pyrex, however, and the arsenic was found after the heating in the form of a solid slug in the lower part of the magnesia powder. It may possibly have come in contact to a slight extent with the iron of the pipe while in the molten condition. A slender rod about 1 mm. square in section and 2 cm. long was worked out of the slug with a file and a hack saw and by grinding. Grooves were filed on the ends, connections made with spring clips, and measurements made with the potentiometer in the regular way. I was surprised to find after I had completed the measurements that Matthiesen [16] had soldered connections to arsenic, and I verified for myself that it is as easy to soft solder to this metal as to antimony, for example. In fact the completely metallic character of the massive casting is a surprise contrasted with the appearance of the sublimed material as ordinarily furnished. Of

course if I ever repeat this work I shall make connections by soldering.

A measurement of the temperature coefficient of resistance showed a discouragingly high probable impurity; the average coefficient between 0° and 95° was 0.00076, whereas Matthiesen [15] had found 0.0038. The high probable impurity of this sample did not make it worth while to make any very extended pressure measurements. One run was made. There were considerable irregularities, but within the limits of error the relation between pressure and resistance is linear to 12000 kg., and the value of the coefficient is -0.0_5326.

This coefficient is similar to that of a number of metals both as regards magnitude and sign. Arsenic is seen therefore to acquire neither the abnormal sign of the coefficient of its neighbors bismuth and antimony on the one side, nor the abnormally high numerical value of the coefficient of black phosphorus on the other.

Liquid Bismuth. The pressure coefficient of resistance of solid bismuth is abnormal in being positive; it was of particular interest to find whether the same abnormal behavior holds for the liquid. The bismuth used for these measurements was from the same lot of electrolytic bismuth as that whose pressure coefficient was previously measured. It was melted into a U-shaped fine glass capillary provided with four sealed-in platinum terminals for use with the potentiometer method. Special precautions were necessary to prevent the bismuth from cracking the capillary on freezing; this was accomplished by very slow cooling from the bottom up after the capillary had been filled with liquid bismuth. In this way congealing ran upward from the bottom of the capillary toward the open top, and no liquid was entrapped by the solid to crack the glass by its expansion on freezing.

A special arrangement of the pressure apparatus was necessary to permit the electrical measurements. The same arrangement was also used with lithium, sodium, and potassium, but since the apparatus was first used with bismuth, it will be described here. The difficulty was with the insulating plug, which was packed with soft rubber. This would have been carbonized by the temperature of melting bismuth. The pressure apparatus was accordingly constructed in three parts, instead of the customary two. There was an upper cylinder, as usual, in which pressure was produced, and in which was located the measuring coil of manganin wire. This upper cylinder was connected by a stout tube with the cylinder below it, in which was placed the bismuth in the glass capillary. This second cylinder was surrounded with a bath of Crisco, by which the desired temperature was maintained by thermostatic regulation. Out of the bottom of the

second pressure cylinder was led another piece of stout tubing, which passed through a stuffing box in the bottom of the Crisco bath, and below the bath connected with a third pressure cylinder. This third cylinder was kept cool by a bath of water at room temperature. This bath was stirred to maintain the temperature uniform, but it was not necessary to regulate the temperature thermostatically. In the lower pressure cylinder was situated the insulating plug, of the same design as used in all the work with the potentiometer method. The plug was connected with the bismuth in the second cylinder by four insulated leads brought down through the pipe connecting the second and third cylinders. The insulation of these wires was asbestos; asbestos covered copper wire is now a commercial product. In this way the insulating plug was kept cool, so that there was no danger of leakage or failure of insulation because of the high temperature. The only trouble to be anticipated was large parasitic e.m.f.'s because of the large differences of temperature, but the parts in which there were temperature gradients were composed of electrically homogeneous material, and no more trouble was found from this effect than at ordinary temperatures.

Runs were made on liquid bismuth at 274.6°, 260.0°, and 239.6°, in this order. For fear of damaging the capillary (fused in platinum leads almost always make trouble under pressure) the pressure was not raised to the maximum of this work, 12000 kg., until the last run, so that I did not obtain data for the resistance of the liquid over the entire possible range. At 239.6°, however, pressure was run to the maximum with no bad effects. After the measurements on the liquid, the bismuth was allowed to freeze under pressure, and measurements were attempted on the solid. The results for the solid were not good, however, probably because of strains introduced on freezing in the fine capillary. There was no way of controlling the freezing under pressure and making it take place from the bottom up as had been possible in initially setting up the apparatus. The effects of strains were apparent in two ways; the pressure coefficient of resistance of the solid was negative over part of the range below the solidifying point, whereas that of the unconstrained solid is positive, and the freezing point was depressed a couple of degrees, which is in the direction to be expected if there are internal strains. Irregularities introduced by these strains are of importance, however, only when it was desired to obtain the relative changes of resistance with changes of pressure, and it was possible to find a value for the change of resistance on solidifaction which should not be greatly in error.

The readings on the liquid went very smoothly. Within the limits of sensitiveness there was no difference between points obtained with ascending or descending pressure, and except for one point, all of the observed points lay on smooth curves within the sensitiveness of reading, which was about 0.2% of the total effect. The observed values, smoothed for temperature and pressure, are shown in Table XIII in terms of the resistance at the melting point at atmospheric pressure as unity. The values tabulated are "observed" values, that is, they have not been corrected for the thermal expansion or

TABLE XIII.

BISMUTH.

Relative Values of Observed Resistance of the Liquid in Glass Capillary.

Pressure kg/cm²	Resistance 275°	260°	240°
0	1.0019		
1000	.9900		
2000	.9789		
3000	.9684	.9617	
4000	.9584	.9520	
5000	.9490	.9426	
6000	.9400	.9336	.9253
7000	.9314	.9249	.9169
8000		.9167	.9088
9000			.9008
10000			.8931
11000			.8855
12000			.8783

The resistance of the liquid at atmospheric pressure and 271.0° is taken as unity.

compressibility of the glass capillary. It did not seem best to do this because of the uncertainty in the values for the glass at the temperatures and pressures of the measurements. The glass used for the capillary was an ordinary soft soda glass. The best value for the cubic compressibility is probably 2.7×10^{-6}, taking Amagat's values for the compressibility and temperature coefficient of compressibility, and for the linear thermal expansion the best value is probably 8×10^{-6}.

The most important result shown by the table is that the pressure coefficient of resistance of the liquid is negative like all normal metals.

The positive coefficient of the solid is therefore presumably due to its crystalline structure. The liquid behaves in other ways also like normal metals. When resistance is plotted against pressure, the curve is convex toward the pressure axis; that is, the pressure coefficient decreases relatively (and also absolutely) at the higher pressures. The pressure coefficient is little affected by temperature, within this range, and also the temperature coefficient is little affected by pressure. The initial pressure coefficient of the "observed" resistance at 275° is -0.0_4123, which corrects, using the constants above, to -0.0_4132 for the specific resistance. Both of these coefficients are to be distinguished from the pressure coefficient of the "observed" resistance of a solid. The pressure coefficient of the liquid is of the same magnitude as that shown by the softer solid metals, such as lead, and is also very nearly the same numerically, although of opposite sign, as that of solid bismuth.

The temperature coefficient of the "observed" resistance at 275° is 0.00047, which corrects to 0.00048 for the coefficient of the specific resistance. This is about five times less than the value for a normal solid at the same temperature. It is almost always true that the temperature coefficient of the liquid is materially less than that of the solid.

At 7000 kg. at the equilibrium point, the resistance of the liquid is approximately 45% of that of the solid. At atmospheric pressure Northrup and Sherwood [17] found for the ratio 43%. There was considerable preliminary rounding of their melting curve, so their results are probably not any more accurate than mine, but it is at any rate evident that this ratio does not suffer any large change with increasing pressure.

TUNGSTEN. In the preceding paper [18] results were given for the pressure coefficient of resistance of tungsten, but the value of the temperature coefficient of resistance of the sample used was so low (0.00322) that it was probable that the tungsten was not very pure. Since the publication of my earlier paper Beckman [19] has measured the effect of pressure to 1600 kg. on the resistance of a sample of tungsten having a considerably higher temperature coefficient than my original piece, and has found a higher initial value of the pressure coefficient than I did.

The sample of tungsten on which I previously experimented was the purest which the General Electric Co. was at that time in a position to offer me. I have since learned that it was probably "doped," that is, thoriated, the impurity of thorium being 0.2 or 0.3%. Through

the kindness of the manufacturers I have since been able to measure the resistance of two samples of "undoped" tungsten of high purity. The Westinghouse Lamp Works gave me a specimen which they estimated to contain less than 0.03% total impurity, and the Research Laboratory of the General Electric Co. placed at my disposal a specimen which they estimated to be even purer. Judging by the test of the temperature coefficient the General Electric sample was appreciably purer. The average temperature coefficient between 0° and 100° of the Westinghouse sample was 0.003925, and that of the General Electric sample 0.004209.

Pressure measurements were made on both samples, but only those on the purer are given in detail here. The treatment of both specimens was the same. The wire was 0.002 inches in diameter; it was wound bare on a bone core, and connections were made by fusing to it pure nickel wire with an arc in hydrogen. This method of making

TABLE XIV.

TUNGSTEN.

Temp. °C.	Resistance	Pressure Coefficient. At 0 kg.	At 12000 kg.	Average 0–12000	Maximum Deviation from Linearity	Pressure of Maximum Deviation
0	1.0000	-0.0_5143	-0.0_5131	-0.0_51346	.00015	5500
50	1.2084	137	133	1340	7	7000
100	1.4209	140	136	1368	14	7500

connections was taught me by the General Electric Co., and is simpler than the combination of gold and platinum which I formerly used, although the former connection was just as satisfactory electrically. The wires were seasoned by a long preliminary heating to 125° and by an application of 12000 kg. Three runs were made, at 0°, 50°, and 95°. Except for two bad points, the greatest departure of any of the observed points from a smooth curve at any of the three temperatures was 0.2% of the total effect, and the displacement of the zero after a run was not greater than the irregularity of the other points. The observed results were smoothed, and a table constructed for the resistance as a function of pressure and temperature by regular methods. The results are shown in Table XIV and Figure 9. The

relation between pressure and resistance is nearly linear, and the departure is in the normal direction, that is, the coefficient becomes less at the higher pressures. The results are somewhat unusual in that the pressure coefficient does not advance regularly with increasing temperature, but is less at 50° than at either 0° or 100°. The same behavior was shown by the impurer sample also, and is doubtless real. The departure from linearity is also less at 50° than at either 0° or 100°.

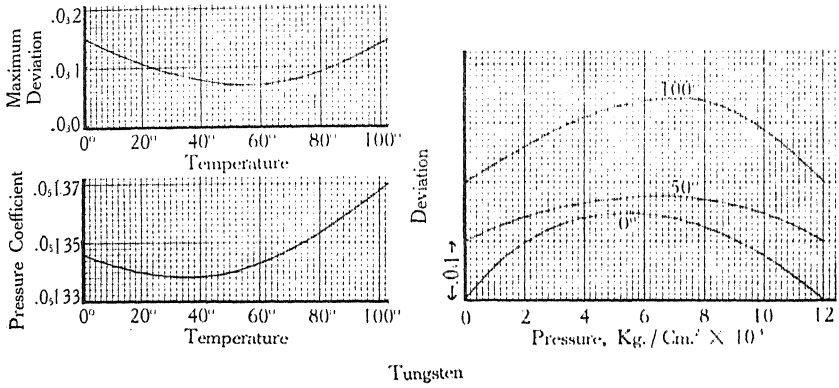


FIGURE 9. Results for the measured resistance of tungsten. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

The results for the impurer sample were similar, but the numerical values were different. The average coefficients to 12000 at 0°, 50°, and 100° being respectively -0.0_51387, 1331, and 1362. These may be compared with the values of the Table; the differences are of the order of 0.5% at 50° and 100°, but the difference rises to 3% at 0°. At 0° the coefficient of the impurer is larger, and at the two other temperatures is smaller.

These results may be compared with those recently published by Beckman.[18] He finds for the average temperature coefficient of his sample 0.00399, which is a trifle higher than that of the impurer sample above. His initial pressure coefficient at 0° is -0.0_5151, reduced from atmospheres as the pressure unit to kg/cm². This value is 2.7% higher than that of the impurer of the two samples above, and 5.6% higher than that of the purer. A comparison of the present results with my former ones shows that both of my new samples,

which are purer than my former one, have a higher pressure coefficient. It is evident that the sign of the effect of impurity on the pressure coefficient cannot be predicted with probability, as can the effect of impurity on the temperature coefficient. At the same time the fact is to be emphasized, previously already found to hold in a number of cases, that the effect of impurity on the pressure coefficient is usually much less than on the temperature coefficient. Thus in the present case, a change in the temperature coefficient of 31% (present compared with former work) is accompanied by a change of pressure coefficient of only 9%.

LANTHANUM. This material I owe to the kindness of Professor Charles Baskerville, who had prepared it from the fused salts by electrolysis. No chemical analysis was available, but a spectroscopic analysis by Professor F. A. Saunders showed a large amount of Mg (possibly 10–20%) and a considerable amount of Si. There was a trace of Ca, no Ba, and none of the other rare earth metals were detected. The rare earths tested for were Ce, Pr, Nd, Er, Y, Yt, Dy, Lu. A nodule about one gram in amount was available for the measurements. A small homogeneous piece was cut from the nodule, and extruded to wire in a small die of special construction. It is necessary to heat to about 450° to extrude, and even then the extrusion is a matter of some difficulty. The wire so formed is exceedingly stiff; it is evident that its elastic constants and its elastic limit are both high. It is quite brittle, and can be bent only into a circle of large radius. I prepared two pieces of wire, one at a somewhat higher extrusion temperature than the other; the mechanical properties seemed unaffected by the temperature of extrusion. The wire on which measurements were made was only 1.7 cm. long, and was that prepared at the lower extrusion temperature. In order to attach the four terminals, spring clamps of special design had to be used; it is not possible to solder this metal. The clamps gave some difficulty with shifting of position, and the results were not so regular as usual.

The temperature coefficient of this material between 0° and 100° was only 0.001476. This is very low, and indicates that the material was not very pure. For this reason it did not seem worth while to spend a great deal of effort on the pressure measurements, although these could have been improved by repeating the measurements with a longer specimen, which was obtained after the easiest extrusion temperature was discovered.

Two runs were made for the pressure coefficient, at 0° and 50°. The ascending points of the run at 0° were entirely regular, but the

descending points were irregular, probably because of slipping of the contacts. At 50° the ascending and descending points agreed more closely, but there were irregularities both ascending and descending, less in magnitude than at 0°, and averaging 2.7% of the maximum pressure effect.

The results are collected in Table XV and Figure 10; they are seen to be quite normal. The pressure coefficient is negative, and

TABLE XV.

LANTHANUM.

Temp. °C.	Resistance	Pressure Coefficient			Maximum Deviation from Linearity	Pressure of Maximum Deviation
		At 0 kg.	At 12000 kg.	Average 0–12000		
0	1.0000	−0.0339	−0.0225	−0.0.0331	.0020	5800
50	1.0752	39	36	377	4	5800
100	1.1476					

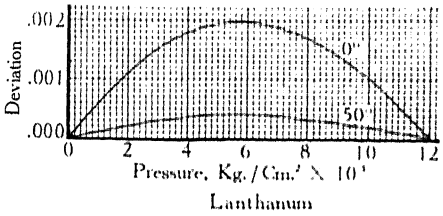


FIGURE 10. The deviations from linearity of the measured resistance of lanthanum in fractional parts of the resistance at 0 kg. and 0°C.

increases at the higher temperatures. The relation between pressure and resistance is also normal, the coefficient being smaller at the higher pressures. It is perhaps unusual that the departure from linearity is less at the higher temperatures. The deviations from linearity are so small and so nearly symmetrical about the mean pressure that it is not necessary to reproduce the deviation curve graphically.

I have been able to find no previous values for the specific resistance of this metal. The approximate value for the specimen above,

obtained from micrometer measurements of its dimensions, was 59×10^{-6} ohms per cm. cube.

NEODYMIUM. This, as well as the lanthanum, I owe to the kindness of Professor Baskerville. Professor Saunders was kind enough to make a spectroscopic analysis of this also. He found a large amount of Mg, a little Si and La, a trace of Ca, no Ba, and nothing else recognizable. He tested for the rare earths Ce, Pr, Y, Yt, Lu, Dy, Er. The form and method of preparation of the specimen was essentially the same as that of lanthanum. It was extruded into wire 0.020 inches in diameter at 450°. The extrusion was materially easier than that of lanthanum. The wire is not so stiff, and may be straightened after extrusion without fear of breaking. Nevertheless it obviously belongs to the metals with high elastic constants and high elastic limit. The specimen used for the measurements was 7.1 cm. in length; the manner of attachment of the connections was the same as with lanthanum. The greater length of the specimen, and perhaps greater skill in handling it, led to much more regular results.

A preliminary measurement of the temperature coefficient was made at 0°, 50°, and 95°. Within this range the relation between temperature and resistance was found to be linear, and the coefficient was 0.000799. This is extraordinarily low, much lower than for lanthanum even, and it did not seem worth while to expend a great deal of time on the pressure measurements.

Two runs were made for the pressure coefficient, at 0° and 50°. The results were rather regular. There was no difference between readings with increasing and decreasing pressure, and the zero was well recovered. The maximum departure of any single point from a smooth curve was 2.6% of the total effect at both 0° and 50°. The numerical results are shown in Table XVI. The values are quite

TABLE XVI.

NEODYMIUM.

Temp. °C.	Resistance	Pressure Coefficient			Maximum Deviation from Linearity	Pressure of Maximum Deviation
		At 0 kg.	At 12000	Average 0–12000		
0	1.0000	-0.0_5238	-0.0_5183	-0.0_5213	.00078	6000
50	1.0400	250	197	226	87	6000

normal. The coefficient is negative, and becomes greater numerically at the higher temperature. The departure from linearity with pressure is in the normal direction, the coefficient being less at the higher pressures. The departure from linearity is symmetrical, a second degree curve accurately reproducing the results, so that it is not necessary to draw the deviation curves. The deviation becomes greater at the higher temperatures, as is normal.

I can find no tabulated values for the specific resistance of neodymium. The value for the specimen above, obtained from micrometer measurements of its dimensions, was 107×10^{-6} ohms per cm. cube, about twice the value for lanthanum.

CARBON. These results on carbon must be regarded as of an entirely tentative and orienting character. Present technical methods are not yet sufficiently perfect to permit of the manufacture of carbon, either amorphous or graphitic, of specifiable or reproducible properties. Any massive form of carbon always contains at least a slight amount of binder of unknown properties, amorphous carbon is always impure with a slight amount of graphite, and the purest graphite contains a small and unknown amount of amorphous carbon.

Experiments were made on three samples of carbon. The first of these was supposedly amorphous carbon, an arc carbon made by an unknown German firm. The second was Acheson graphite cut from a piece of graphite furnished by the Acheson Co. for a resistance furnace, and presumably not made with any unusual precautions. The third specimen of graphite was also Acheson graphite, furnished by the Acheson Co., in response to a special request for graphite of the greatest obtainable purity. It was stated by them to contain the minimum of binder, and to have been graphitized with unusual thoroughness, but otherwise its properties were not known.

In view of the unreproducible character of the results it will not pay to give them in great detail.

Two sets of readings were made on the gas carbon, a complete run to 12000 kg. and back at 30°, and a few readings at 96°. This specimen was about 3.5 inches long, and 0.154 inches diameter. Measurements were made by the potentiometer method, using the three terminal plug as usual. Connections were made to the carbon with spiral springs snapped into grooves filed around the surface of the rod. A preliminary seasoning was made to 6000 kg., but there was very little permanent change of resistance. At 30°, the resistance decreases with rising pressure, and the direction of curvature is normal, that is, the proportional effect becomes smaller at the higher pressures. The

percentage decrease of resistance was 6.68% at 6000 kg., and 12.07% at 12000 kg. At 96°, up to 3000 kg., the coefficient is about 4% greater. The resistance decreases linearly with temperature between 0° and 100°, the total decrease for 100° being 2.56% of the resistance at 0°. The readings on this carbon were entirely regular, showed little difference between ascending and descending values, and an almost perfect recovery of the zero.

The first specimen of Acheson graphite was cut from a rod of 1.5 inches diameter to about the same dimensions as the gas carbon. Measurements were made by the same method. Three complete series of readings were made, at 0°, 51°, and 97.4°. The readings were not so regular as with the gas carbon, showing large hysteresis effects, rising at the maximum to 12% of the total pressure effect, and there were also parasitic e.m.f.'s so large as to necessitate a special arrangement of the constants of the circuit. The sign of the effect is positive, the reverse of what it is for gas carbon, and there is very considerable departure from linearity with pressure, the coefficient becoming numerically less at the higher pressures. The total fractional increase of resistance under 12000 kg. decreases with rising temperature, being 4.75% at 0°, 4.23% at 50°, and 4.23% also at 100°. The large departure from linearity may be judged from the fact that at 6000 kg. at 0° the increase of resistance is 3.44%, which is 72% of the increase under 12000 kg. The resistance decreases with rising temperature at atmospheric pressure, and the change is not linear. At 0° the resistance on an arbitrary scale is 1.0000, at 50° 0.9135, and at 100° 0.8687.

The second specimen of graphite, supposed to be especially pure, was subjected to a special preliminary seasoning in order to eliminate as far as possible the pores. It was sealed into a lead tube and subjected to a fluid pressure of 12000 kg. on the outside of the tube. The diameter of the specimen was reduced by about 2%, but there were a great many pores still visible to the naked eye. It was further seasoned by heating to 125° in vacuum; this treatment should have removed all moisture, of which no traces, however, were evident. This specimen was cut to the same dimensions, and measurements made in the same way as on the two preceding samples. Only one run was made, at 50°. This was terminated by an explosion at 12000 kg. In view of the unreproducible character of the results it did not seem worth while to repeat the effort to obtain a complete set of readings. As with the other sample of Acheson graphite, the effect of pressure is to increase the resistance, but the change was much less

numerically than for the other piece, and
was much greater, suggesting
the resistance may pass through a
of resistance were found at
respectively; namely,
The temperature coefficient of
measured.

Although the results obtained
are not reproducible, two
signs of the pressure coefficient for
graphitic states, and the large
with graphite, indicating a
found in which a maximum or
reached at high pressures.

SILICON. It is well known that
perfect for producing a pure and
carbon. For instance, the
in sign with different pieces of
In view of this situation it
sure measurements in order to
effects. Two specimens were
Electric Co.

The first sample had not
been obtained from the
cylinder about 5 mm. in
made with spring clips,
method, as usual. The
that the irregularities were
were large seasoning effects on the
were always permanent changes of
differences between the readings
sure in a direction the reverse of
made, at 0° and 52°. The
normal. At 0° the total
52° 15.8%. The effect is not
becomes less at the higher
temperature coefficient of this

The second sample was
dum Co., but it had been
by melting in vacuum. The
for it was possible to see with the

and there were numerous fairly large pores. (There were visible pores in the first sample also). It need not be anticipated that the pores cause any error in the pressure coefficient, for the transmitting liquid freely penetrates the pores and transmits pressure uniformly to all parts; there is never any permanent change of dimensions after an application of pressure. The second sample was of approximately the same dimensions and was treated in the same way as the first. Two sets of readings were made with this second sample, at 0° and 95°. The pressure coefficient is negative in sign, as it was for the first sample, but the numerical values are somewhat different. At 0° the resistance decreases by 10.1% under 12000 kg., and at 95° by 15.3%. The change is not linear with pressure, but the coefficient becomes larger at the higher pressures, which is the opposite of the normal behavior of the first sample. The temperature coefficient of this sample between 0° and 95° was $+0.0000615$, about half as large as that of the first sample.

In spite of the very marked differences these two samples agree much more nearly in their pressure coefficients than they do in their temperature coefficients. This agrees with previous experience, that in general the temperature coefficient is much more susceptible to impurity than the pressure coefficient. We may expect, therefore, that the pressure coefficient of resistance of pure silicon will be found to be negative, and of the order of -0.000012, pressure being expressed in kg/cm^2. Compared with most metals, this coefficient is high, being about the same as that of lead.

Black Phosphorus. Runs were made on two samples of this substance. The first was from the same piece as that which gave the values for the specific resistance and temperature coefficient of resistance already published.[20] The method of formation and some of the other properties have also been described. During the six years since the previous measurements, this specimen has been kept in a glass bottle, closed with a cork stopper and sealed with paraffine. The protection from the action of the air was not perfect, however, because the phosphorus had become covered with a layer of moisture. This moisture is probably due to slow oxidation of the phosphorus in the air. The result of oxidation is the formation of phosphoric acid, which is well known to be very hygroscopic, and therefore rapidly absorbs moisture from the air. An attempt was made to remove the acid from the sample by boiling it with water for a number of hours, and then heating in vacuum for a number of hours in addition.

The specimen previously used was a cylinder about 0.5 inches in

diameter. For the resistance measurements a square prism was cut from the center of this about 0.2 inches on a side. The resistance was measured by the potentiometer method, with the three terminal plug. The terminals were attached to the phosphorus by means of helical coils of very fine wire snapped over the prism in grooves filed on its surface. The distance between potential terminals was about 1.5 cm.

One run was made with this sample, at 0°. The points with increasing pressure ran smoothly, and on decreasing pressure the points with increasing pressure were repeated, except the final zero, where there developed a parasitic e.m.f. so large that further readings were impossible. The general character of the pressure effect was an enormous decrease of resistance under pressure. The results before the parasitic e.m.f. appeared were very nearly the same as those found later with the second sample. The parasitic e.m.f. was ascribed to the imperfect removal of the phosphoric acid, and the specimen was again treated for a number of hours with boiling water, but without success. It was evident that the acid permeated the material too deeply to be removed by surface treatment in this way. It was accordingly necessary to prepare a fresh specimen of phosphorus.

In preparing this fresh sample, advantage was taken of an observation made by Dr. A. Smits [21] in preparing the phosphorus for measurements of the vapor pressure. He found that the kerosene by which pressure had been transmitted to the phosphorus during formation was exceedingly difficult to remove. A chemical analysis by Professor Baxter had also shown some carbon as an impurity of the phosphorus; it is possible that some of this might also have been introduced by the kerosene. It was therefore indicated that the black phosphorus should be formed if possible without contact with kerosene. This was simply done by surrounding the yellow phosphorus with water in the lower cylinder, transmitting pressure to the water with kerosene as usual, but so choosing the dimensions that the kerosene should never come in contact with the phosphorus. This was entirely successful; the transition went essentially as before, when kerosene was used. In particular, occasion was taken to again measure the time rate of transition, and the same results found which have already been published,[22] and which make the explanation of the transition from yellow to black phosphorus so puzzling. That the phosphorus formed under water was purer than the phosphorus previously formed under kerosene was suggested by the absence of the peculiar odor, which had permeated the earlier product, char-

acteristic of kerosene which has been exposed to high temperatures and pressures. It would be of interest if the vapor pressure measurements of Professor Smits could be repeated on this specimen.

The specimen so formed was dried in vacuum for a number of hours, at 125°, and sealed into an exhausted glass tube until ready for use. It was cut to the same dimensions, and mounted in the same way as the other specimen. Three runs were made with this, at 0°, 51°, and 95°. In addition to the temperature seasoning incidentally done when it was heated in vacuum, it was given a pressure seasoning by an application of 12000 kg. at 0°. The runs all went smoothly; parasitic

TABLE XVII.

BLACK PHOSPHORUS.

Pressure kg/cm²	Resistance 0°	50°	100°
0	1.000	0.662	0.421
1000	.796	.521	.323
2000	.643	.406	.250
3000	.492	.313	.1950
4000	.372	.239	.1517
5000	.277	.1816	.1183
6000	.2042	.1371	.0910
7000	.1493	.1028	.0701
8000	.1079	.0766	.0542
9000	.0783	.0572	.0425
10000	.0565	.0427	.0337
11000	.0409	.0318	.0266
12000	.0297	.0238	.0209

e.m.f.'s were no larger than would be expected from the high thermal e.m.f. of this material, the behavior was perfectly reversible with ascending and descending pressure, and the alteration of zero after a run was no larger than the irregularities of any other of the observed points.

The outstanding feature of the results is the exceedingly large decrease of resistance brought about by pressure, much larger than for any other substance which I have measured. At 0° and 12000 kg. the resistance is only 3% of its value at atmospheric pressure. The ordinary method of plotting is not adapted to such a wide range

of relative values, and accordingly in smoothing the results and making the interpolations and extrapolations involved in making a table of resistance at uniform intervals of pressure and temperature, the logarithm of the resistance was plotted against pressure instead of resistance itself.

Except for two bad points, the maximum departure of any point from a smooth curve at any temperature was 2% of the resistance at that point, and the agreement was usually much closer.

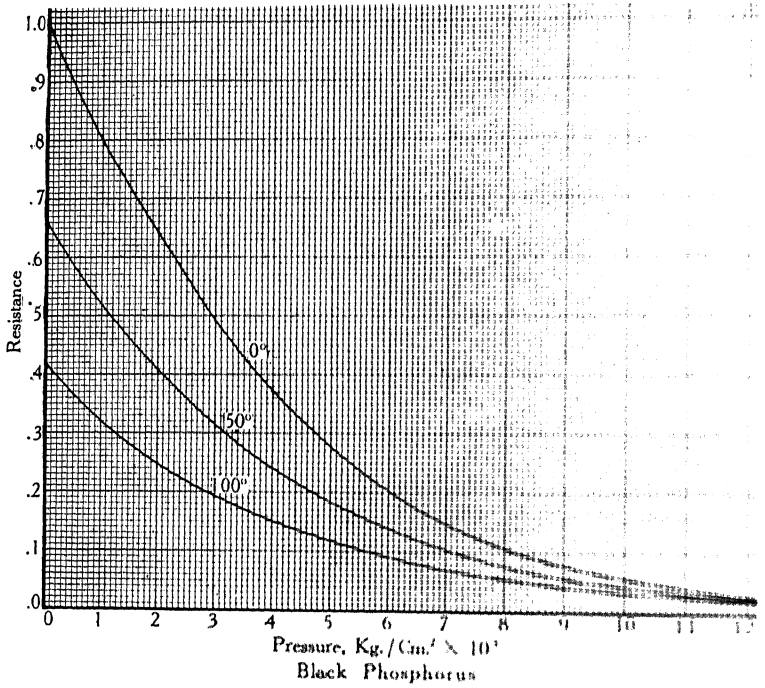


FIGURE 11. Relative resistances of black phosphorus at several constant temperatures as a function of pressure.

The smoothed results are shown in Table XVII, which gives resistance at 0°, 50°, and 100° at even 1000 kg. intervals, and in Figure 11. The use of significant figures in the table should be mentioned, the number of decimal places not being constant throughout the table. The accuracy of the results justifies only the places shown. The

resistance itself was measured at every point with enough accuracy so that it would have been permissible to keep throughout the table a constant number of decimal places, but the pressure itself at the lower pressures is not known with a high enough accuracy to justify keeping more significant figures than shown.

When the logarithm of resistance is plotted against pressure a nearly linear relation is found at all three temperatures. This means that $\frac{1}{R}\frac{dR}{dp}$ is approximately constant at all pressures at constant temperature, where R is the instantaneous value of the resistance at the pressure in question. The instantaneous pressure coefficient is a function of temperature, however. The average value of the instantaneous coefficient between 0 and 12000 kg. is -0.000293 at 0°, -0.000277 at 50°, and -0.000250 at 100°. The deviation of the logarithm from exact linearity changes sign with rising temperature. At 0° and 50° the instantaneous coefficient becomes greater with increasing pressure, which is not what one might expect, whereas at 100° it becomes less. At the two lower temperatures the deviations from linearity run smoothly with the pressure, but at 100° the variations, although much less numerically, show one or two points of inflection with rising pressure. At 0° the initial value of the instantaneous coefficient is -0.000200 and at 12000 kg. it has risen to -0.000320; the corresponding values for 50° are -0.000231 and 0.000290, and for 100° -0.000262 and -0.000249.

The specific resistance was also determined. At 0° this was found to be exactly 1.000 ohms per cm. cube. This is higher than the value previously published for the other specimen, which was 0.711. The effect of temperature on the new specimen is also greater than on the previous one. The values for this specimen are shown in the table. The resistance decreases with increasing temperature, and the effect is not linear, as of course it cannot be, for otherwise the resistance would become zero at some finite temperature. The coefficient found for the other specimen was also negative, but smaller numerically and within the temperature range, the relation was linear. Previously the relative resistance was found to drop from 1.000 to 0.711 between 0° and 50°, whereas here the drop is found to be from 1.000 to 0.622 for the same temperature interval. In view of the greater precautions in the preparation of this sample, there can be no doubt but that the present values are to be preferred.

It was considered of sufficient interest to measure the thermal e.m.f. of this specimen of black phosphorus. The details of the

method need not be described; they were sufficiently obvious. Asymmetry in the specimen was eliminated by making two sets of readings with the hot and cold ends reversed. The difference of readings in the two positions was only 3 %. The temperature interval was from 0° to 21°. The effect is very large. The thermal e.m.f. against copper in this interval was at the rate of 0.000413 volts per degree Centigrade, positive current flowing from copper to phosphorus at the hot junction.

Iodine. The measurements on iodine were part of the systematic attempt to measure the effect of pressure on the resistance of all the elements which could be handled with sufficient ease. The striking effects found for black phosphorus, and the nearness of phosphorus and iodine in the periodic table gave rise to the hope that a similar effect might be found with iodine.

The measurements proved of unexpected difficulty, because of the readiness with which iodine dissolves in most of the liquids by which pressure can be transmitted. It was found, for instance, that iodine dissolves in kerosene, or petroleum ether, or glycerine. It was a surprise to find that the solutions are fairly good conductors. Considerable effort was spent in devising a suitable method of transmitting pressure to the iodine and getting electrical connections into it, but without much success. In the arrangement finally adopted, the iodine was melted into an open glass cup, provided with two platinum electrodes connected with wires sealed through the base. The cup was placed in a second larger cup, and the wires led up between the inner and the outer cup, and bent over the edge of the outer cup. The upper part of the inner cup was filled with water to a sufficient depth to completely cover the iodine. The outer cup was filled with Nujol, which covered the iodine and water in the inner cup. Connections were made as usual to an insulating plug, this time one of the old single-terminal plugs. The object of the double arrangement of cups was to keep the iodine from contact with the oil, and to keep the water from contact with the insulating plug and any part of the leads, which would otherwise have been short circuited. The arrangement was not satisfactory, for the glass cracked around the platinum leads under pressure, allowing a slight amount of iodine to go into solution in the oil, and furthermore, because of unequal compressibility of the glass and iodine, some water crept between the surface of the glass and the iodine, thus making a short circuit possible. The iodine further dissolved to some extent in the water under pressure, and from the water it again diffused into the surrounding oil, so that there

was a second possibility of short circuit. The initial resistance of the arrangement was of the order of one megohm. Pressure was not pushed higher than 8000 kg., in order not to freeze the water. At this pressure the resistance had dropped to 35000 ohms. There were large polarization effects, and on releasing pressure the resistance did not recover its initial high value.

These experiments can only justify the conclusion, therefore, that under high pressure iodine does not at any rate become metallic in its conductivity, but the specific resistance remains high. It is quite possible that the relative resistance may suffer large changes, but the probability is small that the change of relative resistance is as high as it is for black phosphorus.

The iodine used for this experiment was Kahlbaum's, previously dried in vacuum. The platinum electrodes were approximately 1 cm^2 each in area, and 3 mm. distance from each other. These dimensions, together with the value of the minimum resistance recorded above, allow a minimum value to be set for the specific resistance at 8000 kg. of about 100,000 ohms per cm. cube. The correct value is doubtless many fold greater. The specific resistance of iodine under ordinary conditions seems too much affected by impurities to allow of its accurate determination, and I have not been able to find a value anywhere recorded.

"CHROMEL A." This is an alloy for high temperature resistance units essentially similar to the alloys known more familiarly under the name of "Nichrome." "Chromel A" is made by the Hoskins Co. of Detroit, and has the composition 80% nickel and 20% chromium. It was furnished by the manufacturer in the form of a wire 0.005 inches diameter, and was double silk covered by the New England Electrical Works. I wound it for these measurements into a coreless toroid of 118 ohms resistance at 0°. It was seasoned for the measurements by keeping it at 135° for four hours, and by a preliminary application of 2000 kg.

The effect of pressure is in the normal direction, that is, the resistance decreases with increasing pressure, but the effect is very small, smaller than any which I have previously found. The maximum displacement of the slider of the Carey Foster bridge was 4 cm., so that the sensitiveness of the measurements was not greater than one part in 400. Within the limits of error the relation between pressure and resistance is linear to a maximum pressure of 12000 kg. At 0° the two points at the highest pressures were irregular, probably because of viscosity in the transmitting medium, and at 90° there were hysteresis effects amounting to 4% of the total pressure effect.

At 0° the pressure coefficient was -0.0_6134, and at 90° -0.0_6137. The temperature coefficient between 0° and 90° was 0.000163.

"CHROMEL B." This alloy is much similar to "Chromel A." It is made by the same concern, and has a composition of 85% nickel and 15% chromium. Like the previous material it was furnished in the form of wire 0.005 inches in diameter, and was double covered with silk insulation by the New England Electrical Works. It was also wound into a coreless toroid of approximately 100 ohms resistance at 0°. It was seasoned for temperature at the same time as the "Chromel A" by four hours at 135°, but was in addition seasoned for pressure by a single application of 12000 kg. at room temperature, and a single application of 2000 kg. after mounting ready for the measurements.

The general character of the results is the same as for "Chromel A." The coefficient is not quite so small, and the results were considerably more regular. This was in part due to the choice of a less viscous transmitting medium. The relation between pressure and resistance is linear within the limits of error. Two series of measurements were made, at 0° and 95°, to a maximum pressure of 12000 kg. At 0° the maximum departure of any single reading from the linear relation was 1.5% of the maximum effect, and at 95° it was 1.9%, except for the zero, which showed a displacement of 3.5%.

At 0° the average pressure coefficient was -0.0_6158, and at 95° -0.0_6169. The average temperature coefficient of resistance at atmospheric pressure between 0° and 95° was 0.000212.

"CHROMEL C." This alloy is also intended for high resistance heating units. It is made also by the Hoskins Co., but unlike Chromel A and B contains some iron in addition to nickel and chromium. The exact composition is Fe 25%, Ni 64%, and Cr 11%. The wire was 0.005 inches in diameter, double silk covered, and wound into a coreless toroid of such dimensions as to have at 0° a resistance of 178 ohms. It was seasoned by one preliminary application of 12000 kg., and after connecting to the pressure apparatus by three applications of 2000 kg. Measurements were made on the Carey Foster bridge, as usual with materials of high resistance.

Three runs were made, at 0°, 52.24°, and 95.88°. The variation of resistance is not throughout linear with pressure and temperature, but shows departures in abnormal directions. The departures from linearity do not run uniformly, so that it was not possible from the three series of readings to construct a table of resistance which could be used by interpolation to obtain the resistance to the limit of accuracy at any temperature and pressure within the range. This alloy would merit further study for its own sake, but an elaborate investi-

gation did not fall within the present program, and the results are given as found.

At 0° the relation between pressure and resistance is linear within the limits of error. The maximum departure of any point from the linear relation was 0.3% of the total pressure effect, and the departures from linearity were distributed at random. The average pressure coefficient of resistance between 0 and 12000 kg. was -0.0_64272.

At 52.24° the relation between pressure and resistance was again linear within the limits of error, but there was sensible hysteresis. The maximum width of the hysteresis loop was 1% of the total effect. The ascending and descending points all lay smoothly on their respective branches of the hysteresis loop without departures of more than 0.06% of the effect. The average pressure coefficient between 0 and 12000 kg. was -0.0_64194, less than the value at 0°.

At 95.88° the relation between pressure and resistance was sensibly not linear, but could be represented within the limits of error by a second degree curve. The maximum departure of any observed point from the second degree curve was 0.35% of the maximum effect. The departure from linearity is in the abnormal direction, that is, the average coefficient between 0 and 6000 is less numerically than the average coefficient between 0 and 12000 kg. The average coefficient 0 to 12000 was -0.0_64488, and that between 0 and 6000 was -0.0_64372. It is to be noticed that somewhere between 0° and 100° the pressure coefficient of resistance has passed through a minimum.

The temperature coefficient of resistance at atmospheric pressure is normal in being positive, but the direction of curvature is abnormal. The average coefficient between 0° and 52° is 0.001076, and between 0° and 96° 0.001030.

"Comet" Alloy. This is an alloy of the following composition:

Cr	1.75%
Ni	31–32%
C	.20–.25%
Si	.20–.25%
Mn	1.8–2.0%
P and S	very low
Fe	balance

It is made by the Electrical Alloy Co. and was furnished by them in the form of wire 0.005 inches in diameter, and doubly covered with silk insulation. It was wound for the measurements into a coreless toroid of 283 ohms resistance at 0°. Readings were made on the Carey Foster bridge in the usual way at 0°, 51.22°, and 95.32°.

The wire was seasoned by a preliminary application of [illegible] room temperature, and after soldering to the manganin plates [illegible] additional applications of 2000 kg. at room temperature. That the seasoning was adequate is shown by the fact that there was no perceptible change of zero after the first excursion to 1 000 and back.

The readings showed a small but distinct hysteresis, more [illegible] the higher temperatures. At 0° the width of the loop [illegible] total pressure effect, at 51° 0.5% of the effect, and at 95° [illegible]. At 95° there was a displacement of the zero after the run of an amount equal to the width of the hysteresis loop. At the other temperatures there was no perceptible change of zero.

The results were computed in the usual way, and are shown in Table XVIII, and Figure 12. This alloy is unusual in that the pres-

TABLE XVIII

"COMET" ALLOY

Temp. °C.	Resistance	Pressure Coefficient			Pressure of Max. Hysteresis	Max. Hysteresis
		At 0 kg.	At 12000	Average		
0	1.00000	+0.0,2263	0.0[illegible]	0.0[illegible]	[illegible]	[illegible]
50	1.04644	224	206	215	[illegible]	[illegible]
100	1.09061	203	194	200	[illegible]	[illegible]

sure coefficient of resistance becomes less at the higher temperatures, although the resistance itself becomes greater. The behavior is normal in that the pressure coefficient becomes less at the higher pressures at constant temperature. The relation between pressure and resistance becomes more nearly linear at the higher temperatures, which would be unusual for a pure metal.

"THERLO." This is an alloy much like manganin in its properties, made by the Driver Harris Co. The composition is Cu 84%, Mn 12%, Al 2%. It has been used in the high pressure work at the Geophysical Laboratory as a substitute for manganin in high pressure gauges. The sample on which I made measurements was 0.005 inches in diameter, double silk covered, and wound into a coreless toroid of a resistance at 0° of 127 ohms. This was very nearly the resistance of

the manganin pressure gauge, so that a very accurate comparison of the pressure coefficients of manganin and Therlo could be made by plotting on a large scale the difference of the readings with the two alloys. The Therlo was seasoned by one application of 12000 kg. at room temperature, and after soldering to the insulating plug, by four additional applications of 2000 kg.

Three runs were made, at 0°, 51.05°, and 94.80°. The variations with temperature were so slight that the readings could be reduced to regular temperature intervals by an interpolation or extrapolation so short that there was no possibility of error. The resistance of this sample of Therlo did not vary quite linearly with pressure, that is,

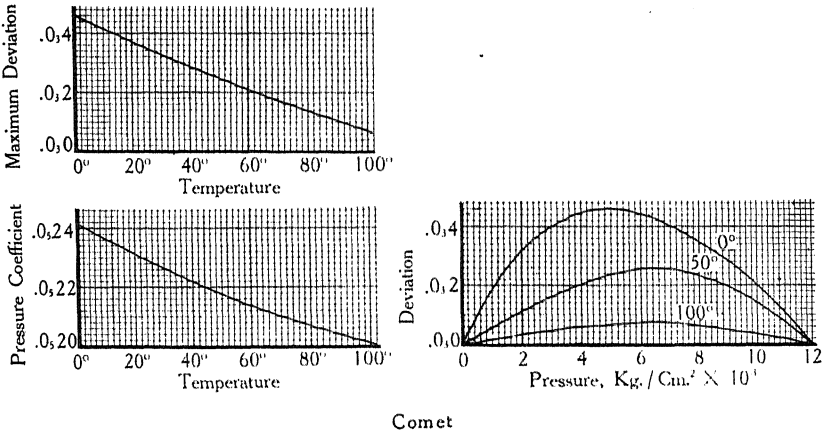


FIGURE 12. Results for the measured resistance of Comet alloy. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

it did not vary linearly with the manganin. (The manganin was originally calibrated against an absolute gauge and found linear within 0.1%). The deviations from linearity of the Therlo are greatest at the lower pressures and are not symmetrical.

At 0° the maximum departure of any single observed point from a smooth curve was 0.09% of the total pressure effect, at 51° 0.14%, and at 95° 0.05%.

The results have been computed in the regular way, and are exhibited in Table XIX and Figure 13. The method of representation is the same as that used in the preceding paper on resistance under

TABLE XIX.

"THERLO."

Temp. °C.	Resistance	Pressure Coefficient			Maximum Deviation from Linearity	Pressure of Maximum Deviation
		At 0 kg.	At 12000	Average 0–12000		
0	1.00000	+0.0$_5$2361	+0.0$_5$2273	+0.0$_5$2283	.000112	4000
50	1.00120	2386	2318	2308	112	4500
100	1.00104	2367	2320	2323	83	5000

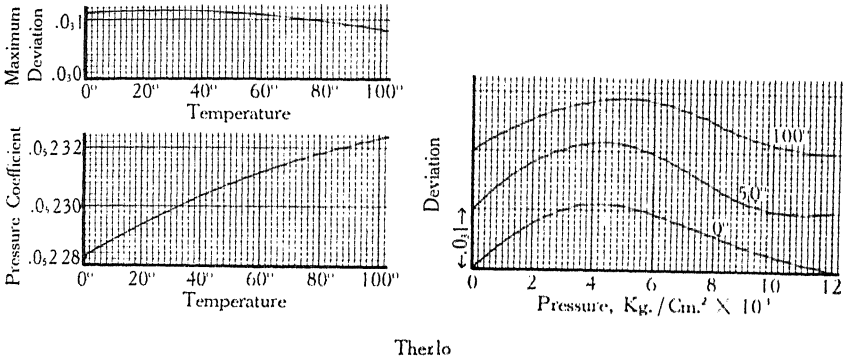


FIGURE 13. Results for the measured resistance of Therlo alloy. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 1200 kg.

pressure. It will be noticed that the average pressure coefficient shows greater variation with temperature than does that of manganin, and the variations are in fact greater than the variations of resistance itself. The resistance passes through a maximum in the neighborhood of 75°, the increase between 0° and 75° being 0.120%, and between 0° and 100° 0.104%, whereas the average pressure coefficient continues to increase over the entire range between 0° and 100°. The instantaneous coefficient at 0 kg., however, passes through a maximum between 0° and 100°.

"#193 ALLOY." This is an alloy containing Fe 68%, Ni 30%, and

Cr 2%, made by the Driver Harris Co. for use in heating units. I was interested in the pressure and temperature coefficients because I had used it as the capillary for containing liquid lithium. The accuracy required in the coefficients was not high, so that measurements of the pressure coefficient at only one temperature and of the temperature coefficient between only two temperatures were sufficient.

The specimen was in the form of a capillary 0.045 inches outside diameter, and 0.032 inches inside diameter, about 6 cm. long. The resistance was too low to be measured by the Carey Foster method, and accordingly the potentiometer was used, as with other metals of low resistance. The temperature of the pressure readings was 94.2°. At this temperature the resistance decreases with increasing pressure, the relation is linear within the limits of error, and the average coefficient between 0 and 12000 kg. is -0.0_51790. Except for a single bad point, the maximum departure of any reading from the linear relation was 0.7% of the total effect, and the arithmetic mean of all the departures was 0.25%.

The average temperature coefficient of resistance at atmospheric pressure between 0° and 94° was 0.000684.

General Survey of Results.

We have in the first place to inquire whether these new results for elements somewhat unusual in their properties are the same in character as those previously obtained for the more common elements. In discussing the new data it will be convenient to discuss separately metals in the solid and liquid state, and also metals with positive or negative pressure coefficients of resistance. The previous results were almost entirely for solid metals; measurements for only one liquid metal, mercury, had been made at that time. Furthermore, the pressure coefficient of all solids, except bismuth and antimony, was negative. In the following a solid or liquid is called normal if its pressure coefficient of resistance is negative. The alloys will require separate discussion.

Normal Solids. The normal solids embraced in the present series of measurements are Na, K, Mg, Hg, Ga, Ti, Zr, As, W, La, Nd, Si, and black phosphorus. The special interest of these measurements attaches to those substances with large coefficients. Many of the above list do not belong in this category, and may be dismissed with a few words.

Mg and W were measured in the previous paper. Except for the improvement in the numerical values afforded by the new measurements, these substances require no further discussion. It is to be noticed that the revised values of the pressure coefficient are in such a direction as to make the pressure coefficients of atomic amplitude and resistance even more divergent than was found previously.[1]

La and Nd are the first metals of the rare earth group whose pressure coefficients of resistance have been measured. The coefficients of both these substances are not distinguished in any particular way over those of the elements of the previous paper, and do not require further discussion.

Ti and Zr also belong to a class of elements not previously measured. There was considerable impurity in these materials, and the results have no considerable accuracy. The results are chiefly remarkable for the smallness of the coefficients, which are smaller than for any other pure substances measured. It is even possible that Ti belongs to the abnormal metals, and that its resistance increases with increasing pressure, but the experimental accuracy was not high enough to allow this to be stated with certainty.

Arsenic is a substance which might be expected to show abnormal results because of its position in the periodic table, but it is actually found to be quite normal both in regard to the sign of the coefficient and its magnitude.

Gallium is another substance for which abnormal results were expected because of its anomalous property of expanding on freezing. The coefficient is however, normal in sign and magnitude. The accuracy of the measurements was not great enough to give the variation of the pressure or temperature coefficients over the range open to measurement.

Solid mercury has been here measured for the first time over a restricted range. It is quite normal with regard to sign and size of the coefficient.

Silicon and phosphorus are non-metallic in character, and will be discussed later. This leaves of the above list of normal metals only the alkali metals sodium and potassium as needing special comment because of the magnitude of their coefficients. Of the metals previously studied lead was found to have the greatest coefficient, the resistance under 12000 kg. being 14% less than under atmospheric pressure. Contrasted with this is a decrease of over 40% in the resistance of sodium and over 70% in that of potassium under a pressure of 12000 kg. The question is whether substances with such high coefficients

show any change in the usual types of behavior formerly found. The principle facts found before for normal metals were: (1) The pressure coefficient is little affected by temperature, (2) The temperature coefficient is little affected by pressure within the range, and (3) the instantaneous pressure coefficient decreases with increasing pressure (the maximum change in the instantaneous coefficient was that of lead which changed about 30% under 12000 kg.).

Sodium and potassium show no such constancy of behavior, as might be expected from the high values of their compressibilities and pressure coefficients of resistance. Thus for sodium the values of the instantaneous pressure coefficients $\left[\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau\right]$ at 0° at 0, 6000, and 12000 kg. respectively are -0.0_4663, 0.0_4435, and 0.0_4268, a total decrease by a factor of 2.49. At 80° the corresponding coefficients are -0.0_4786, 0.0_4466, and 0.0_4307, a total decrease by a factor of 2.56. This is a little larger than the factor of decrease at 0°, which is what one would expect. A comparison of corresponding pressure coefficients at 0° and 80° shows the pressure coefficient of sodium is by no means independent of temperature, but the change in the pressure coefficient with temperature is less than the change in resistance itself. The mean temperature coefficient of resistance may also be found from the table of resistance of sodium, and is 0.00475 at 0 kg., and 0.00408 at 12000 kg. The relative change is much larger than that found previously for any of the other metals, but still is not large compared with the variations of the pressure coefficient over the same range of pressure.

The same sort of phenomena are seen to characterize potassium, although the coefficients are not known over so wide a range as are those of sodium. At 25° the instantaneous pressure coefficients of resistance at 0, 6000, and 12000 kg. respectively are 0.0_3186, 0.0_4955, and 0.0_471, a decrease by a factor of 2.62. At 95° the pressure coefficients at 6000 and 12000 kg. are 0.0_31024 and 0.0_4885, and at 165° the coefficient at 12000 kg. is 0.0_31027. The pressure coefficient therefore increases markedly with increasing temperature. The mean temperature coefficients between 25° and 60° at 0, 6000, and 12000 kg. respectively are 0.00454, 0.00341, and 0.00184. The decrease is relatively much larger than for sodium, and is nearly as large as the relative decrease in the pressure coefficient over the same range.

The alkali metals sodium and potassium differ, therefore, in the following particulars from the metals previously measured. The

instantaneous pressure coefficient increases with rising temperature and decreases with rising pressure by amounts which, for the range of this work, may amount to a factor between 2 and 3. The temperature coefficient of resistance decreases with increasing pressure by very perceptible amounts, and decreases much more for potassium than sodium.

The decrease in temperature coefficient at the higher pressures is especially significant. One might perhaps expect that at higher pressures the metal would be compressed into an approach toward its behavior at 0° Abs under atmospheric pressure, since the volume may be reduced by pressure to less than its value at 0° Abs. Now as the absolute zero is approached at atmospheric pressure the temperature coefficient of resistance becomes much greater than the reciprocal of the absolute temperature; this is the exact opposite of the behavior found above at high pressures, the temperature coefficient becoming less. The effect of increasing pressure is seen to be merely that of making the part played by temperature of less and less relative importance, which is after all not unnatural from a certain point of view. In the absence of specific information to the contrary it is natural to connect the unusual behavior of sodium and potassium with the large change of volume, and to expect that other metals will show the same sort of behavior under correspondingly increased pressures.

The non-metals Si and P would not be expected to agree in behavior with the metals, but it is interesting, nevertheless, to summarize their behavior. The magnitude of the mean coefficient of Si is about the same as that of lead. The coefficient may increase very largely with increasing temperature, however, and also may apparently increase with increasing pressure. This is quite contrary to expectations, and would seem to indicate an approach to some sort of instability at high pressures; perhaps as the atoms are pushed more closely together there is an approach to metallic conductivity. The variations of the temperature coefficient of silicon are also abnormal. Initially the coefficient is normal in sign, but small numerically; as pressure is increased it reverses in sign. This reversal in sign of the temperature coefficient, unlike the behavior of the pressure coefficient, does not indicate an approach to metallic conductivity. Too great weight should not be attached to these results, because the silicon was impure. However, it is evident that there are some interesting possibilities here, and the measurements should be repeated when it is possible to obtain purer material.

Black phosphorus is remarkable for the great magnitude of the

coefficient, the resistance decreasing to only 3% of its initial value under 120000 kg. In spite of this abnormally large effect, the relative variation with pressure of the pressure coefficient is much less than that of sodium or potassium. The figures have already been given. There is a reversal of behavior with rising temperature. At 0° and 50° the instantaneous pressure coefficient increases with rising pressure, which is not what we would expect, but at 100° the coefficient falls with rising pressure. The temperature coefficient of black phosphorus is abnormal in sign, being negative. The coefficient decreases numerically with rising pressure, at first slowly, but more and more rapidly. From the table of resistance it may be found that the mean temperature coefficient between 0° and 100° are — 0.00579, 554, and 299 at 0, 6000, and 12000 kg. respectively. The readings at the higher pressures are not so accurate as the others, so that possibly the rate of fall of the coefficient at high pressures may be too rapid.

Abnormal solids. Previously there were measurements on only two abnormal solids, bismuth and antimony. The results for antimony were not sufficiently accurate to show the variation of pressure coefficient with pressure, but except for this the two metals agreed in that the pressure coefficient increases with increasing pressure and falls with increasing temperature, and the temperature coefficient falls with increasing pressure.

The instantaneous pressure coefficient of lithium increases with rising pressure, having the following values at 0, 6000, and 12000 kg. respectively; 0.0_568, 0.0_574, and 0.0_5796. The accuracy of the measurements was not sufficient to establish variations of pressure coefficient with temperature, or of temperature coefficient with pressure within the range. So far as the results are certain, however, the behavior of Li is like that of Bi and Sb.

For calcium the following values may be found from the table of resistance. The instantaneous pressure coefficients at 0° have at 0, 6000, and 12000 kg. the respective values 0.0_4106, 0.0_4121, and 0.0_4135. The corresponding values at 100° are 0.0_592, 0.0_4107, and 0.0_4119. The pressure coefficient therefore increases with increasing pressure, and decreases with rising temperature. The average temperature coefficients of resistance between 0° and 25° are 0.00299, 0.00291, and 0.00281 at 0, 6000, and 12000 kg. respectively, thus decreasing with rising pressure. Within the limits of error the temperature coefficients between 75° and 100° are the same as between 0° and 25°. It would be normal for the temperature coefficients to decrease with rising temperature. In all particulars of comparison, therefore, Ca is like Bi and Sb.

The pressure coefficient of strontium is abnormal. At 0° the instantaneous coefficient varies only little with increasing pressure, but what change there is is a decrease, which is abnormal. The range of values is from 0.0_4503 to 0.0_4492. At 50° the pressure coefficient at first increases with rising pressure, which is what we have come to regard as normal for this type of substances, but between 2000 and 3000 kg. passes through a flat maximum, and from there on decreases. The range is from 0.0_4469 to 0.0_4451. At 100° the behavior is like that at 50° except that the maximum with pressure is very much more pronounced, and the maximum occurs at 7000 kg. At 100° the initial value of the instantaneous coefficient is 0.0_4351, the maximum at 7000 is 0.0_4452, and at 12000 kg. it has dropped to 0.0_4432. There is, however, nothing abnormal in the temperature coefficient. The average temperature coefficients between 0° and 100° are 0.00383, 0.00311, and 0.00275 at 0, 6000, and 12000 kg. respectively. In respect therefore to the variation of pressure coefficient with temperature and temperature coefficient with pressure strontium is like the other metals with positive coefficient, but the variation of pressure coefficient with pressure is like that of the others over only a part of the range. It is to be remarked that the absolute value of the pressure coefficient of strontium is much higher than that of any other metal.

Summarizing, the behavior of the five abnormal metals, with the exception of the pressure variation of the pressure coefficient of strontium, is alike in that the instantaneous pressure coefficient increases with rising pressure and decreases with rising temperature, and the temperature coefficient falls with rising pressure.

Carbon, in the form of graphite, is the only other element at present known with a positive pressure coefficient of resistance. Since it is not metallic, comparisons are unprofitable. Furthermore, it was not possible to obtain results that were numerically reproducible. It may be worth mentioning, however, that graphite is like the metals above in that the pressure coefficient decreases with increasing temperature, but that it is different in that the pressure coefficient is very much less at the higher pressures.

Normal Liquids. The only liquid metal previously measured was mercury. It was found for it that the instantaneous pressure coefficient decreases with rising pressure and increases with rising temperature, and that the temperature coefficient decreases with rising pressure and rising temperature. The behavior is in all respects that which appeals to us as normal. It is worth while to give the

numerical values for liquid mercury, since the range of the previous measurements has now been considerably extended. The results are shown in Table XX.

TABLE XX.

Liquid Mercury.

Temperature	$-\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_t$		
	0 kg.	6000 kg.	12000 kg.
0°	0.0$_4$522	0.0$_4$239	
50°	340	253	
100°	367	227	
	Average Temperature Coefficient		
0–25°	0.00096	0.00074	
75–100°	90	65	0.00054

The measurements on liquid sodium did not cover so wide a range as those on liquid mercury, but within the range they show the same characteristics. At 200° the instantaneous pressure coefficients at 0, 6000, and 12000 kg. respectively are 0.0$_4$922, 0.0$_4$594, and 0.0$_4$396. The relative decrease with rising pressure is considerably greater than is the case with mercury, and furthermore, the coefficient itself is considerably greater. The mean temperature coefficient between 180° and 200° is 0.00325 at 0 kg., and 0.00244 at 12000 kg. This decrease is relatively not so large as that of mercury, although the coefficient itself is larger.

Potassium was liquid over a still smaller range than sodium, so that it is not possible to give as complete results. The instantaneous pressure coefficient decreases with rising pressure, the values at 165° being 0.000168 and 0.000136 at 0 and 6000 kg. respectively. The average temperature coefficient between 135° and 165° increases from 0.00322 at 0 kg. to 0.00463 at 5000 kg., which is the reverse of the behavior of liquid sodium and mercury. The variation with temperature of the pressure coefficient is also abnormal. The initia

pressure coefficient of the liquid at 62.5° is 0.0_326, and at 165° this has dropped to 0.0_317.

Liquid gallium shows a rather large decrease of the instantaneous pressure coefficient with rising pressure. At 30° the values of the coefficient at 0, 6000, and 12000 kg. respectively are 0.0_540, 0.0_535, and 0.0_490. At 100° the corresponding values are 634, 541, and 491. The effect of temperature on the pressure coefficient is therefore relatively slight; at the lower pressures the coefficient decreases with rising temperature, and at the higher pressures it decreases. The mean temperature coefficient of resistance between 30° and 100° changes relatively little, being 0.000815, 829, and 808 at 0, 6000, and 12000 kg. respectively. Compared with sodium and potassium the changes of all the coefficients of gallium are relatively small. It is to be remarked also that the pressure coefficient of gallium is of the same order of magnitude as that of many solid metals; we have come to expect relatively slight variations of the coefficients of those substances with small coefficients.

Liquid bismuth was measured over only part of its region of stability, so that again complete results are not at hand. At 275° the instantaneous pressure coefficient drops from 0.0_4123 at 0 kg. to 0.0_591 at 6000 kg., and at 240° the coefficient is 0.0_592 at 6000 kg., and 0.0_580 at 12000. The temperature coefficient of resistance at 275° drops from 0.00047 at 0 kg. to 0.000453 at 6000 kg. Liquid bismuth is therefore entirely normal in all respects, that is, a falling pressure coefficient with rising pressure and falling temperature, and a falling temperature coefficient with rising pressure. This complete normality is in spite of the fact that solid bismuth is abnormal in having a positive pressure coefficient. The presumption is therefore very strong that the abnormality of the solid is mainly due to the crystalline structure. It is known of course that bismuth crystallizes in the hexagonal system which is not normal, nearly all the elements being cubic.

Summarizing, except for potassium, the behavior of all these liquid metals is of the same type; the pressure coefficient decreases with rising pressure and increases with rising temperature, and the temperature coefficient decreases with rising pressure.

Abnormal Liquids. Only one abnormal liquid, that is, a liquid with a positive pressure coefficient of resistance, is known, liquid lithium. For this the relation between pressure and resistance was linear within the limits of error and the coefficient was independent of temperature between 200° and 240°. A linear relation between

resistance and pressure means a pressure coefficient becoming less at the higher pressures. This is what one might at first expect, but this is the first time that we have found it in a substance with positive coefficient. Since the pressure coefficient is independent of temperature, the temperature coefficient is independent of pressure over the range of the measurements.

Relative Behavior of the Same Metal in the Solid and the Liquid States. This is a matter of considerable importance as suggesting the relative parts played in the mechanism of conduction by the crystalline structure and the properties of the atoms as such. It will in the first place pay to recall the fact already well known that the direction in which the resistance changes when a metal melts is also the direction in which the volume changes. If the metal expands on melting, as is normal, the specific resistance increases on melting, and if the metal expands on freezing, the resistance of the liquid is less than that of the solid. This rule is without exception. Gallium and bismuth are the only two metals known at present in the second class; the data for antimony do not as yet seem well established. In the present work I was able to add lithium to the list of substances which obey this rule. This is of interest, because solid lithium is abnormal.

With regard to the magnitude of the change of resistance on melting there have been a number of theoretical proposals. The inaccuracy of the experimental results has allowed considerable latitude here. Thus theoretical considerations have been based on the assumption that the ratio of the resistance of the solid to that of the liquid is approximately an integer.[23] There is perhaps a tendency for the values to cluster about the figure 2, but it is now certain that within the limits of error the ratio is not integral. Attempts have been made to connect quantitatively the volumes of solid and liquid with the resistance, as would be suggested by the above general rule. Thus Professor Hall [24] has suggested that if the resistance of the solid is extrapolated to such a temperature that the volume expansion is sufficient to bring the volume of the solid up to the volume of the liquid at the melting temperature, the resistance of the solid will be found to be the same as that of the liquid. Of course any such long-range extrapolation must always be open to question, and it is probable that the numerical agreement found is no more significant than the general rule relating to volume already mentioned.

The above measurements under pressure bring out a fact that could not have been known before, namely that the ratio of the resistance of solid to liquid is approximately a constant characteristic of the

particular substance, which does not change greatly as pressure and temperature are changed along the melting curve. We now have the figures for the ratio of the resistance of solid to liquid for six metals at different pressures and temperatures. For lithium the accuracy was not high enough to permit more than the statement that the ratio does not change greatly in a pressure range of 8000 kg. For sodium the ratio is 1.45 at atmospheric pressure, and has dropped to 1.36 on the melting curve at 12000 kg. The difference of volume between solid and liquid has dropped to half its initial value in the same pressure range, so that the ratio of resistances is evidently more constant than the difference of volume. For potassium the ratio of resistance of liquid to solid is 1.56 at 0 kg., and has dropped only to 1.55 at 9700 kg. Contrasted with this almost negligible change in the ratio of the resistances is a decrease under 9700 kg. of the difference of volume between solid and liquid to 0.31 of its initial value. For mercury, I determined the ratio of resistance of liquid to solid at the melting point at 0° and 7640 kg. to be 3.345. I did not make measurements at any other temperature but there are values by other observers. Onnes [25] finds 4.22, Bouty and Cailletet [26] 4.08, and Weber [27] gives 3.8 as the mean of six determinations, all for the ratio at the freezing point at atmospheric pressure. The error is so large that it is not possible to say more than that the change in the ratio along the melting curve is not large, and is in the direction of a decrease with increasing pressure. The change is probably greater than the change in the difference of volume between solid and liquid, which is abnormally constant for mercury, there being a decrease in the difference of only 1% over the pressure range of 7640 kg. The change in the resistance of the liquid over this range is, however, 19%, which is probably larger than the change in the ratio of the resistance of liquid to solid.

The behavior of the two abnormal metals gallium and bismuth is similar. At 7000 kg. I found the ratio of the resistance of liquid to solid bismuth to be 0.45, and at atmospheric pressure Northrup and Sherwood [16] found 0.43. The ratio is probably constant within the limits of error. For Gallium I found 0.58 for the ratio at atmospheric pressure, and calculated the value at 12000 kg. to be 0.61. This again is perhaps to be regarded as constant within the limits of error, but it is noteworthy that the little variation there is is in the same direction for both gallium and bismuth, and is toward an increase with rising pressure, whereas what variation there was for normal metals was always in the direction of a decrease with rising pressure.

We now compare the relative magnitudes of the pressure and

temperature coefficients of solid and liquid. With regard to the temperature coefficients at atmospheric pressure it has long been known that the coefficient of the liquid is less than that of the solid. This is verified for all the metals measured here, except potassium.

With regard to the pressure coefficient of resistance it is natural to expect that of the liquid to be greater than that of the solid at the same temperature. This is true for sodium. At 120° the pressure coefficient of the liquid is about 7% greater than that of the solid extrapolated to the same temperature. It is however, perhaps surprising that the relative change of the pressure coefficient of solid sodium brought about by an increase of pressure of 12000 kg. is greater than that of the liquid under the same increase of pressure. The relative decrease of the temperature coefficient under 12000 kg. is greater for liquid sodium, however, than for the solid.

The behavior of liquid potassium is not as we would expect. At the melting point at atmospheric pressure the pressure coefficient of liquid potassium is greater than that of the solid. Because of the abnormal temperature coefficient of the pressure coefficient of the liquid, however, the coefficient of the solid would become greater than that of the liquid if the solid could be superheated sufficiently. The relative variation with pressure of the pressure coefficient is greater for the solid than the liquid. This again is not what we might expect. The data for potassium do not cover a sufficient range to permit a comparison of the variation with pressure of the temperature coefficients of solid and liquid.

The pressure coefficient of solid mercury has been found to be constant over the range from 7640 to 12000 kg. The coefficient of the liquid, on the other hand, decreases with rising pressure. It has already been mentioned as surprising that the coefficient of the solid is greater than that of the liquid at 6500 kg. This difference would become still more accentuated if the liquid could be carried in the metastable state into the region of stability of the solid; in this range its pressure coefficient would be found to vary considerably less than that of the solid. The measurements were not accurate enough to permit a comparison of the variations of the temperature coefficients of the solid and liquid. It is known, however, that at atmospheric pressure the temperature coefficient of the solid is normal, while that of the liquid is abnormally low even for a liquid.

The pressure coefficient of solid gallium is of the order of 2.5 less than that of the liquid. The coefficient of the solid is independent of the pressure, whereas that of the liquid decreases markedly with

increasing pressure. Measurements were not made on the variation with pressure of the temperature coefficient of the solid.

Comparison cannot properly be made between liquid and solid bismuth, because the solid is abnormal and the liquid is normal. It is interesting, however, that numerically the coefficient of the solid is greater than that of the liquid. This may mean that some of the tendency to abnormality still persists in the liquid, making its coefficient lower than it would otherwise be.

Lithium is abnormal in both liquid and solid. If the data for the solid are extrapolated from 100° to the melting temperature at 180° the figures given would indicate a pressure coefficient of the solid numerically less than that of the liquid. The difference would be still further accentuated if the unknown correction for the compressibility of the solid is applied so as to make the coefficients of both solid and liquid the coefficients of specific resistance. Although the coefficient of the liquid is greater than that of the solid, its variation with pressure is much less, and in fact is opposite in sign, the coefficient of the liquid becoming smaller at higher pressures, and the coefficient of the solid becoming greater. The temperature coefficient of liquid lithium is independent of pressure to 12000 kg., as is that of the solid also.

Summarizing the relations between the coefficients of the liquid and the solid, except for the temperature coefficient of the liquid being less than that of the solid, there does not seem to be a tendency to any one type of behavior. It is noteworthy, however, that in many cases the resistance of the liquid responds more sluggishly to changes of pressure than does that of the solid, the coefficient of the liquid being actually less than that of the solid, or else the change of coefficient with pressure being less for the liquid.

Alloys. The above data on alloys are entirely unsystematic and fragmentary, so that it is not possible to draw any conclusions as to the behavior of alloys in general. It is interesting to notice, however, that the pressure coefficient of all the alloys, with the exception of that of "Comet," is less numerically than would be computed by the law of mixtures from the coefficients of its components, and in the case of "Therlo" this tendency to a lower value may go so far as to reverse the sign. In making this statement I have assumed that the pressure coefficient of pure Chromium and Manganese is negative, a conclusion which has not been checked by experiment, but which seems very probable from the behavior of similar metals.

Theoretical Bearings.

Since the purpose of this paper is primarily the presentation of new data, I cannot more than touch on two matters of theoretical interest suggested by considerations of the previous papers.

It has been known for some time that the temperature coefficient at constant volume of liquid mercury is negative instead of positive, as is the coefficient at constant pressure. In my previous theoretical paper [22] I suggested reasons for this. It is now of interest to find whether the other liquid metals have the same property.

The coefficient of resistance at constant volume is given by the relation

$$\left(\frac{\partial w}{\partial \tau}\right)_v = \left(\frac{\partial w}{\partial \tau}\right)_p - \left(\frac{\partial w}{\partial p}\right)_\tau \frac{\left(\frac{\partial v}{\partial \tau}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_\tau}$$

Hence in addition to the pressure and temperature coefficients of resistance, which have been determined in the present work, values of the thermal expansion and compressibility are also needed. These have not been determined experimentally for any of the metals above, but in some cases an indirect estimate may be made with the help of various data from the melting curve. I have previously given an estimate of the difference of compressibility and thermal expansion between solid and liquid sodium, potassium, and bismuth.[28] With these data, the temperature coefficients at constant volume may be computed, as is shown in Table XXI. The fundamental data are

TABLE XXI.

The Temperature Coefficient at Constant Volume of Liquid Metals at their Melting Points.

Substance	$\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau$	$\frac{1}{v}\left(\frac{\partial v}{\partial \tau}\right)_p$	$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau$	$\frac{1}{w}\left(\frac{\partial w}{\partial \tau}\right)_p$	$\frac{1}{w}\left(\frac{\partial w}{\partial \tau}\right)_v$
Sodium	-0.0_4186	$+0.0_3344$	-0.0_488	$+0.00325$	$+0.00170$
Potassium	-0.0_4358	$.0_3340$	-0.0_3204	0.0044	$+0.0025$
Bismuth	-0.0_532 (?)	$.0_312$ (?)	-0.0_412	0.000475	$+0.0_415$

exceedingly uncertain, because in addition to the uncertainties in the differences of compressibility and thermal expansion between solid and liquid, the compressibilities and thermal expansions of the solids themselves at the melting points are in doubt, the actual measurements having been made in most cases only at room temperature. I have had to guess what the temperature variation of the compressibility might be. However, the uncertainty cannot be so large as to change the sign of the effect for sodium and potassium, for which there can be no doubt that the temperature coefficient at constant volume, as well as the coefficient at constant pressure, is positive. This is the reverse of the behavior of mercury. The data for bismuth are in much more doubt, however. Assuming the figures shown, the coefficient at constant volume is also positive, but the uncertainty is so great that the sign might well be negative.

The coefficient at constant volume of liquid lithium is of course positive, since the pressure coefficient at constant temperature is abnormal in being positive. The data are not at present known for gallium, so that it is not possible to make any sort of an estimate as to the probable value of its coefficient at constant volume.

The outcome of this investigation, therefore, for the only two metals for which the results can be sure, is to reverse the behavior previously found for liquid mercury. In this connection it is to be remarked that the temperature coefficient at constant pressure of liquid mercury is abnormal in being very low, and the corresponding coefficients of liquid sodium and potassium are abnormal in being very high. It does not yet appear, therefore, what the probable value of the constant volume coefficient would be for the more usual metals, such as lead.

The second point of theoretical interest brought out in the previous discussion was the intimate connection between the changes of resistance and the amplitude of atomic vibration.[22] It appeared that the relative change of resistance, whether brought about by a change of pressure or of temperature, was approximately equal to twice the relative change of amplitude under the same change. The relation was by no means exact, there being failures by as much as a factor of two in some cases, but on the average the agreement was rather good for a large number of metals. The question is whether these new elements also show the same relation?

In making the computation the following formula for the change of amplitude with pressure was used

$$\frac{1}{a}\left(\frac{\partial a}{\partial p}\right)_T = -\frac{1}{C_v}\left(\frac{\partial e}{\partial T}\right)_p,$$

where a is atomic amplitude, and C_v specific heat at constant volume per unit volume. It is therefore necessary to know the thermal expansion and specific heats of the new elements. Unfortunately the data are not known for a number of the metals of this work. The computation has been made for all those normal substances for which the data are available, and the results are collected in Table XXII.

TABLE XXII.

Comparison of the Changes under Pressure of Resistance and Amplitude of Atomic Vibration.

Substance	$\frac{1}{v}\left(\frac{\partial v}{\partial \tau}\right)_p$	C_v Kg. cm./cm.^{3}	$\frac{2}{\alpha}\left(\frac{\partial \alpha}{\partial p}\right)_\tau$	$\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_\tau$
Solid Na, 20°	0.0_3217	11.1	-0.0_439	-0.0_468
Liquid Na, 98°	$.0_3344$	10.6	-0.0_465	-0.0_491
Solid K, 20°	$.0_3248$	6.48	-0.0_476	-0.0_5186
Liquid K, 63°	$.0_3341$	6.64	-0.0_3102	-0.0_526
Liquid Hg, 0°	$.0_3181$	17.1	-0.0_6211	-0.0_4358
Arsenic	$.0_416$	26.7	-0.0_512	-0.0_533
Magnesium	$.0_478$	17.7	-0.0_588	-0.0_548
Tungsten	$.0_4101$	27.6	-0.0_674	-0.0_5143

In this table are included the recomputed values for Mg and W. The best agreement is for liquid bismuth. In nearly all the other cases the computed value is much lower than the observed. This is a reversal of the behavior shown by the previous substances, for which in the majority of cases the computed value was too high.

The table seems to show no essential difference between a solid and a liquid metal as far as the connection with amplitude goes.

There seems to be no reason to modify the previous conclusion, which was that in a large way the changes of amplitude of atomic vibration are an exceedingly important factor in affecting changes of resistance. Superposed on this large effect common to all metals, are specific effects, such as peculiarities of atomic structure or arrange-

ment. In particular the factor of atomic arrangement is responsible for the difference between a solid and a liquid metal, and may be so important in some cases as to control the sign of the effect.

Summary.

In this paper results are given for the effect of pressure and temperature on the resistance of twenty elements and several alloys. Endeavor was made to choose elements from unusual places in the periodic table, and also to investigate more fully the behavior of liquid metals.

The resistance of the same metal in the liquid and the solid state has now been measured for six elements. The temperature coefficient of the liquid is less than that of the solid except for potassium. The change of resistance on melting invariably follows the direction of the change of volume. The ratio of resistance of liquid to solid is approximately constant along the melting curve, although the difference of volume may change greatly. The pressure coefficient of the liquid is in some cases less than that of the solid. Liquid bismuth has a negative pressure coefficient of resistance, and is normal, but liquid lithium has a positive coefficient, and is the only such liquid metal yet found. The new liquids do not show a negative temperature coefficient of resistance at contant volume, as did liquid mercury.

The alkali metals sodium and potassium are remarkable for the large changes of resistance under pressure. The pressure coefficient decreases greatly with increasing pressure, and decreasing temperature. The temperature coefficient may decrease greatly with increasing pressure. The variations of these coefficients for the metals investigated in the previous paper were always small.

Three more solid elements have been found with positive pressure coefficients of resistance; lithium, calcium, and strontium. Of these the pressure coefficient decreases with increasing temperature, the temperature coefficient decreases with increasing pressure, and, except for strontium, the pressure coefficient increases with increasing pressure.

Of the non-metallic elements, black phosphorus is remarkable for a very large negative coefficient, the resistance under 12000 kg. dropping to only 3% of its initial value; silicon has a negative coefficient which becomes numerically larger with increasing pressure, and carbon has a negative coefficient in the amorphous state, and a positive coefficient in the graphitic state, which decreases greatly with increasing pressure.

The additional evidence from these new materials still gives every reason to think that the amplitude of atomic vibration is the largest single factor in determining the changes of resistance under pressure or temperature.

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I regret that through an inadvertence on my part I stated in the first of these papers that the previous work of Lisell and Beckman contained a source of error due to the permanent closing of the battery current. Dr. Beckman has been so kind as to call to my attention that this error was present only in the preliminary work of Lisell, and was not present at all in the final results of Lisell, or in any of his own results.

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ON THE X-RAY ABSORPTION WAVE-LENGTHS OF LEAD ISOTOPES

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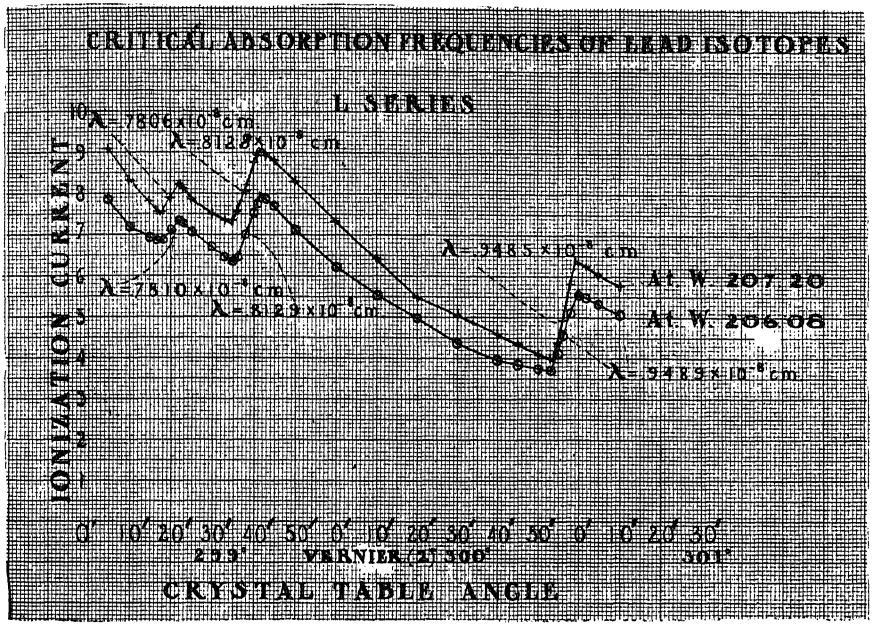
Communicated by T. Lyman, April 5, 1919

Researches on the transformations of radioactive substances have lead to the conclusion that chemical elements exist which have the same atomic number but different atomic weights. Such chemical elements have been called isotopes. In the reactions of ordinary chemical analysis isotopes behave in identically the same manner. It has not been found possible to separate isotopes from each other by means of purely chemical processes; although it seems probable that, since the atomic weights of isotopes differ from each other, they will act somewhat differently in those phenomena in which the mass of the atom enters

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chemical isotopes, also appear to be identical to a very high degree of precision, and recently Siegbahn and Stenström found no difference between their emission spectra in what is called the L series of X-rays.

The object of the research reported in this note has been to investigate the X-ray absorption spectra of chemical isotopes. In general each chemical element, except perhaps those of low atomic numbers, has several critical absorption frequencies, one connected with its K series and three connected with its L series of X-rays. These critical absorption frequencies mark points in the X-ray spectrum where sharp changes in the absorption of X-rays by the chemical element occur. The chemical element absorbs X-rays of higher frequency than the critical frequency to a much greater extent than it does X-rays of lower frequency.



In measuring the critical absorption frequencies of lead isotopes we have used the X-ray spectrometer described in the *Physical Review* for December 1917, page 624. A calcite crystal reflected the X-rays whose wave-length is given by the equation

$$\lambda = 2\,a \sin\theta = 6.056 \sin\theta \times 10^{-8} \text{ cm.}$$

(where θ is the grazing angle of incidence) into an ionization chamber. The ionization method of detecting the reflected beam of X-rays is far superior to the photographic method, both because, if properly used, it requires no correction for the penetration of the X-rays into the crystal, and also because it

The absorbing screen of lead was placed between the X-ray tube and the spectrometer. Professor Richards' laboratory kindly furnished us with the specimens of lead salts. Professor Richards has made accurate measurements of the atomic weights of lead isotopes, and the values he obtained for the two specimens we used were 207.20 for the ordinary lead and 206.08 for the radioactive lead. These differ from each other by more than $\frac{1}{2}\%$.

In our experiments the X-rays came from a molybdenum target tube of the Coolidge type, and a constant difference of potential amounting to about 36,000 volts drove a current of 2 milliamperes through it.

The curves in the figure represent the ionization currents as functions of the readings of one of the verniers attached to the crystal table.

The three sharp drops in each curve correspond to the three critical absorption wave-lengths belonging to the L series of X-rays of each specimen of lead respectively. To get the grazing angles of incidence to substitute in the above formula for the wave-length we measured from the centres of the drops to the zero, 291° 55′ 40″, the value of which has been corrected for eccentricity.

The values of the wave-lengths, etc., have been collected together in the following table.

ABSORBING SCREEN	ATOMIC WEIGHT	$\lambda \times 10^8$ CM.	$\lambda \times 10^8$ CM.	$\lambda \times 10^8$ CM.
Ordinary lead	207.20	0.9485	0.8128	07.806
Radioactive lead	206.08	0.9489	0.8129	0.7810

The grazing angles of incidence can be estimated to within about 30″ of arc, which means that the wave-lengths are correct to within about 0.1%. Corresponding wave-lengths for the two specimens in the above table do not differ from each other by as much as 0.1%, and, therefore, the critical absorption wave lengths of the isotopes of lead are identical to within the limits of error of the experiments.

The magnitude of the characteristic absorption can be estimated from the drops in the curve. These depend, of course, upon the thickness of the absorbing layer, and its measurement is very much less accurate than that of the wave-length. It appears, however, that the relative change of absorption at the three critical wave-lengths is about the same for each isotope of lead.

[Reprinted from the PHYSICAL REVIEW, N.S., Vol. XXIV, No. 1, July, 1919.]

ON THE RELATION BETWEEN THE K SERIES AND THE L SERIES OF X-RAYS.[1]

BY WILLIAM DUANE AND TAKEO SHIMIZU.

SYNOPSIS.—The object has been to measure both the emission and the absorption wave-lengths in the K and L-series characteristic of a chemical element (tungsten), using the same X-ray spectrometer throughout, to see if general relations among them could be found. Graphs have been drawn representing the ionization currents as functions of the crystal table angle. The peaks in these graphs corresponding to the lines α_1 (strong) and α_2 (medium) appear completely separated from each other, although the difference between their wave-lengths amounts to only 2.2 per cent. There is also faint evidence of a third (very weak) line, α_3.

A sharp drop in the absorption graph occurs near the γ line in the K-series corresponding to the K-critical absorption wave-length, and three sharp drops (a strong, a medium and a weak one occur near the L-series, indicating three critical absorption wave-length in that series. The critical absorption frequencies calculated from these graphs are, for the K-series: $\nu = 1.680 \times 10^{19}$; and for the L-series, $\nu_1 = .2438 \times 10^{19}$ (strong), $\nu_2 = .2773 \times 10^{19}$ (medium), $\nu_3 = .2917 \times 10^{19}$ (weak). The frequencies calculated from the peaks representing the emission lines are $\nu_{\alpha_1} = 1.437 \times 10^{19}$ (strong), $\nu_{\alpha_2} = 1.405 \times 10^{19}$ (medium) $\nu_{\alpha_3} = 1.39 \times 10^{19}$ (?) (weak). The precision of measurement is such that the probable error amounts to less than 1/5 per cent.

It appears from these data that to within 1/5 per cent. $\nu - \nu_1 = \nu_{\alpha_1}$ (strong), $\nu - \nu_2 = \nu_{\alpha_2}$ (medium) and $\nu - \nu_3 = \nu_{\alpha_3}$ (weak); in other words *each K α emission line frequency equals the difference between the K critical absorption frequency and one of the L critical absorption frequencies* to within the limits of experimental error. If this law, that *an emission frequency equals the difference between two critical absorption frequencies* applies to all emission lines we must assume critical absorption frequencies in the M series, etc. Two critical absorption frequencies lying between $\nu = 4 \times 10^{17}$ and $\nu = 5 \times 10^{17}$ taken together with those mentioned above will explain the presence of the β line in the K-series and six of the emission lines in the L series, etc.

1. In the analysis of X-rays about sixteen lines have been found to belong to the characteristic spectrum of each chemical element. Usually, although illogically, these have been divided into two series, the K series and the L series. The K series contains at least four lines, known as the α_1, α_2, β and γ lines, of which the γ line has the highest frequency. These four lines belong together in the sense that none of them can be produced by itself. As we increase the voltage V applied to the X-ray tube none of these lines appear in the spectrum until the voltage V reaches the value given by the quantum equation

$$Ve = h\nu, \qquad (1)$$

where e is the charge on the electron h Plank's action constant and a frequency at least as high, and possibly slightly higher than that of t γ line. When the critical voltage has been reached, all four lines appe together; and their intensities increase in approximately the same rat if the voltage is raised still higher.[1]

The above is not true of the L series as a whole. In this series the are at least two and probably three groups of lines, the lines in ea group being connected together in much the same way as are the lin in the K series.[2]

In the analysis of the X-ray absorption spectra of the chemical elemen there appears to be only one critical absorption frequency connecte with the K series. This frequency lies close to and probably slightl above that of the γ line. Within the limits of experimental error equals the frequency that must be substituted in the quantum equatio (1) to give the energy of the electron required to produce the K series

In the absorption spectra of uranium, thorium, bismuth and gold D Broglie found three critical absorption frequencies characteristic of eac element and in the neighborhood of its L series. The writers hav found three such critical frequencies in the absorption spectra of both lead and tungsten. Doubtless these three absorption frequencies belong respectively to the three distinct groups of lines in the L series.

It appears, therefore, from purely experimental evidence that we may divide the known lines in the X-ray spectra of a chemical element into four groups, one in the K series and three in the L series, each group containing a critical absorption frequency and about four emission lines. The lines in each group are connected together in some way, but the relation between their frequencies is not given by the equation

$$\nu = \nu_0 \left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2} \right)$$

in which ν_0 is a constant, and τ_1 and τ_2 are small whole numbers.

The question now arises: Is there any relation between the various groups of lines? Some years ago Kossel suggested that the difference between the frequencies of the α and β lines in the K series might be equal to the frequency of one of the strong lines in the L series, and considerable discussion on this point has appeared in the literature expecially in connection with the theories of the mechanism of X-ray emission spectra and of the structure of the atom. It is evident, however, that this relation cannot be a general relation, for there are many more lines in the L series than in the K series.

[1] See D. L. Webster, PHYS. REV., June, 1916, p. 599, and June

The authors have undertaken the research reported in this paper for the purpose of measuring both the absorption and the emission frequencies with the same apparatus, to see if a more general relation between the frequencies can be found.

We have used the X-ray spectrometer previously described,[1] with a calcite crystal, the formula for the wave-length λ being

$$\lambda = 2a \sin \theta = 6.056 \times \sin \theta \times 10^{-8} \text{ cm.}$$

where θ is the grazing angle of incidence. The X-rays passed through two narrow slits in thick lead blocks before striking the crystal thus obviating a large correction for the absorption of the X-rays in the calcite, as previously explained (*l. c.*). The X-ray tubes were of the Coolidge type, one of them having a tungsten and the other a molybdenum target.[2] The currents passing through these came from a high tension transformer with a system of condensers and kenotrons attached to it for producing approximately a constant difference of potential.

The curves in Fig. 1 represent the K lines of tungsten in both the first and second order spectra. The constant difference of potential applied to the tube amounted to about 100,000 volts in this experiment. The α lines were measured on both sides of the zero line of the spectrometer thus obviating a direct determination of the zero point. A correction of about 45″ of arc must be subtracted from the double grazing angle on account of the excentricity of the spectrometer scale.

There appears to be a somewhat better definition of the lines on the right hand side of the zero line than on the left. Doubtless this is due to a slight lack of uniformity in the crystal structure.

The two α lines on the right hand side appear to be completely separated from each other, even in the first order spectrum. This gives an idea of the precision with which the wave-lengths can be estimated, the difference between the two α wave-lengths being about 2.2 per cent. The position of each peak can be estimated to within 10″ of arc. Since the double grazing angles are about 4°, this means that the error of measurement is less than 1 part in 1,000, unless the same error is made on both sides of the zero line.

The peaks corresponding to α_2 are somewhat unsymmetrical, the slopes on the long wave-length sides being slightly more extended than on the short wave-length sides. This lack of symmetry suggests the presence of an additional line α_3 (?) close to and on the long wave-length side of α_2. Its wave-length should be about $.214 \times 10^{-8}$ cm. To the left of the β

[1] PHYS. REV., December, 1917, p. 624.

[2] Dr. W. D. Coolidge kindly sent us these tubes.

line appears a sharp drop in the curve. This marks the position of t
critical absorption wave-length in the K series. The angular breadth
the drop about equals that of one of the peaks, namely 2′ of arc, and t
angle corresponding to the center of the drop was used in calculating t
critical absorption wave-length.

In this experiment the rays did not pass through an absorbing scre

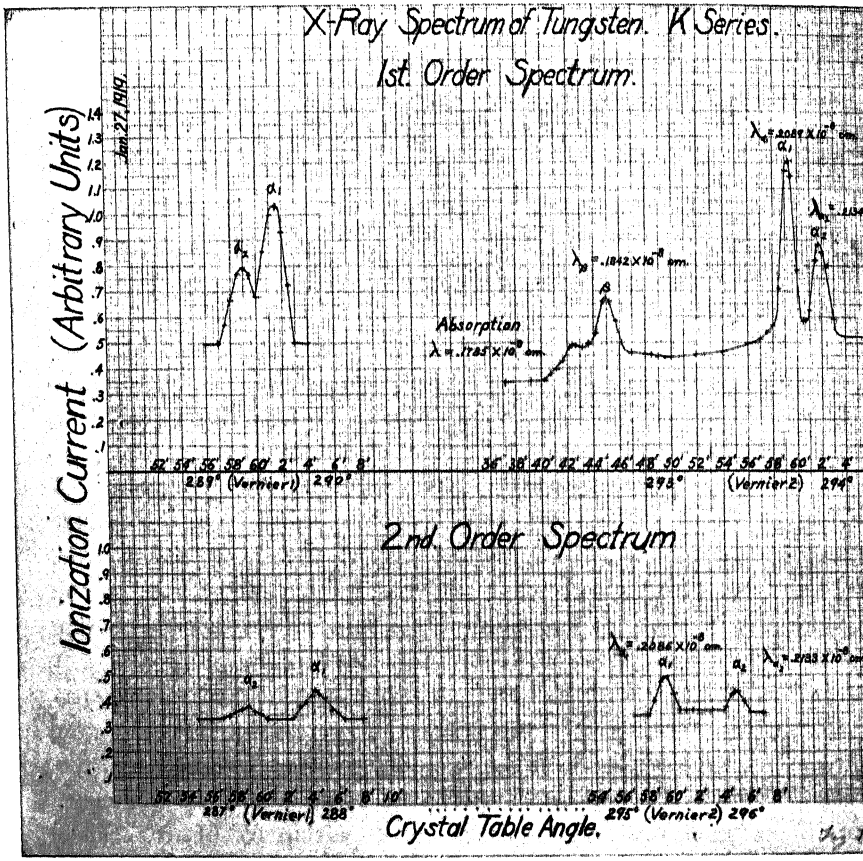


Fig. 1.

of tungsten outside of the X-ray tube, and the reason why the absorp
drop appears in the curve is that we placed the X-ray tube in suc
position that the rays passing through the spectrometer slits came f
the target in a direction almost parallel to its surface. Under t
conditions, since some of the rays are produced slightly below the sur
of the target, part of them is absorbed by the surface layers of the ta
and by any irregularities there may be on the surface.

We have also measured the critical absorption wave-length in th

series using an X-ray tube with a molybdenum target, and placing a layer of sodium tungstate between the tube and the spectrometer as an absorbing screen. In this way we obtained the following values for the wave-length: $\lambda = .1786 \times 10^{-8}$ cm. in the first order spectrum, and $\lambda = .1784 \times 10^{-8}$ cm. in the second order spectrum.

The critical absorption wave-lengths in the L-series of tungsten were measured as follows:

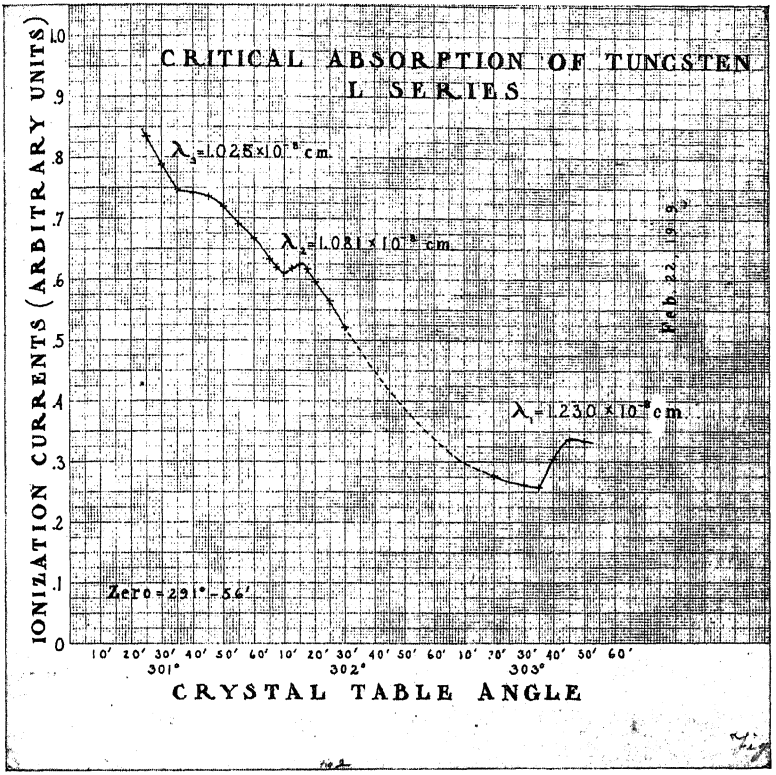


Fig. 2.

The curve in Fig. 2 represents the current in the spectrometer's ionization chamber as a function of the readings of one of the verniers attached to the crystal table in an experiment in which the X-rays came from a molybdenum target and passed through a *thin* layer of sodium tungstate before reaching the spectrometer slits. The three breaks in the curve correspond to the three critical absorption wave-lengths of tungsten that lie in the neighborhood of its L series of emission lines.

We determined the zero on the scale by taking readings on both sides

of the zero line. The value of the zero point given in the figure contains the correction for eccentricity.

The amount of X-ray energy that passes through the glass walls of the X-ray tube in the region corresponding to these long waves is quite small, and we, therefore, had to widen the spectrometer slits somewhat in order to measure the ionization currents. As a consequence the angular breadth of the drops in the curve have increased to four or five times the breadth of the drop in the K series curves. This has not increased the percentage error of the measurements, however, for the grazing angles of incidence in the L series are five to seven times as large as those in the K series.

In this experiment the constant difference of potential between the electrodes of the X-ray tube amounted to about 24,000 volts.

The following table contains the frequencies of vibration calculated from the critical absorption wave-lengths in the K and the L series of tungsten, and also from the wave-lengths of the α and β emission lines of its K series.

Critical Absorption Frequencies.

K Series	*L Series*
1st order spectrum $\nu = 1.680 \times 10^{19}$	$\nu_1 = .2438 \times 10^{19}$ strong,
1st order spectrum $\nu = 1.679 \times 10^{19}$	$\nu_2 = .2773 \times 10^{19}$ medium,
2d order spectrum $\nu = 1.681 \times 10^{19}$	$\nu_3 = .2917 \times 10^{19}$ weak.
Average $\nu = 1.680 \times 10^{19}$	

Emissi n Frequencies.

β-line	α-lines
$\nu_\beta = 1.628 \times 10^{19}$	$\nu_{\alpha_1} = 1.437 \times 10^{19}$ strong.
	$\nu_{\alpha_2} = 1.405 \times 10^{19}$ medium.
	$\nu_{\alpha_3} = 1.39 \times 10^{19}$ (?) weak.

In searching for a general relation between the emission frequencies and the critical absorption frequencies the idea immediately presents itself that an emission frequency may be the difference between two absorption frequencies. The fact that the L series contains three critical absorption frequencies, (a strong, a medium and a weak one), and that there are at least two α emission lines (a strong and a medium one), and possibly a third weak one, lends weight to the idea. From the frequencies contained in the above table we have

$\nu - \nu_1 = 1.436 \times 10^{19}$ (strong), $\nu_{\alpha_1} = 1.437 \times 10^{19}$ (strong),

$\nu - \nu_2 = 1.403 \times 10^{19}$ (medium), $\nu_{\alpha_2} = 1.405 \times 10^{19}$ (medium),

$\nu - \nu_3 = 1.388 \times 10^{19}$ (weak). $\nu_{\alpha_3} = 1.39 \times 10^{19}$ (?) (weak).

It appears from this data, that as a matter of fact *each α line frequency equals the difference between the* K *critical absorption frequency and one of the* L *critical absorption frequencies* to within the limits of experimental error.

If this law applies to all emission lines we must assume the existence of one and perhaps more critical absorption wave-lengths lying between $\lambda = 6 \times 10^{-8}$ cm. and $\lambda' = 7.5 \times 10^{-8}$ cm. (the M series) in order to explain the presence of the β-line in the K series. Two critical absorption wave-lengths lying in this M region taken together with the three critical absorption wave-lengths in the L series explain, according to the law, the presence of 6 of the lines in the L emission series.

The γ line in the K series and several lines in the L series lie very close to the critical absorption wave-lengths, and in order to explain them we must assume the existence of other critical absorption wave-lengths in the suspected N series, etc.

In conclusion we call attention to the fact that the equations which have been suggested to represent the lines in ordinary spectrum analysis are usually in the form of the difference between two functions, and also that X-ray critical absorption is not the same as ordinary absorption which obeys Kirchhoff's law.

HARVARD UNIVERSITY,
March, 1919.

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ON THE CRITICAL ABSORPTION AND CHARACTERISTIC EMISSION X-RAY FREQUENCIES.

BY WILLIAM DUANE AND KANG-FUH HU.

SYNOPSIS.

In the analysis of X-ray line spectra it is of considerable importance to know whether or not the critical absorption, the critical ionization and the highest characteristic emission frequencies associated with any one single X-ray series are exactly equal to each other. Such knowledge must have a marked influence on speculation and theories as to the mechanism of X-radiation and the structure of atoms.

The object of the research reported in this paper has been to measure these three frequencies, as precisely as possible, using the same instruments throughout the work. The measurements have been made with the X-ray spectrometer employed several years ago to determine the value of h. The X-rays came from the steadiest sources at present available, namely, Coolidge tubes excited by currents from a high tension storage battery.

As results of our research we conclude *that the critical ionization frequency equals the critical absorption frequency to within considerably less than 1/10 per cent.*; and that *the critical absorption frequency exceeds the frequency of the γ line in the emission series by 1/4 per cent. or 1/3 per cent.*, these being determined by measuring from the *centers* of the drops and peaks in the curves corresponding to them respectively.

IN the analysis of characteristic X-ray spectra we recognize four different kinds of frequency of vibration associated with each series of lines. In the K series of a chemical element, for example, we have: (*a*) several emission frequencies; (*b*) one critical absorption frequency; (*c*) one critical ionization frequency and (*d*) one frequency such that when it is multiplied by Planck's action constant, h, the product equals the minimum energy the electron in the X-ray tube must have in order that it may be able to produce the K emission series.

It is known that the highest frequency in the emission spectrum (the γ line) and the other three frequencies (*b*), (*c*) and (*d*) lie close together, *i.e.*, within a few per cent. of each other.

The object of the research reported in this paper has been to determine whether, within the limits of experimental error, the γ line frequency the critical absorption frequency and the critical ionization frequency, are exactly equal to each other or not.

[1] A paper presented at the New York meeting of the American Physical Society, April 27, 1918.

Throughout these experiments we used the same X-ray spectron (namely that described in the PHYSICAL REVIEW for December, page 624), and, in order to eliminate some of the possible source error, we did not change the general set up of the instrument.

We calculated the wave-lengths of the X-rays reflected from surface of the calcite crystal by means of the equation

$$\lambda = 6.056 \times \sin\theta \times 10^{-8} \text{ cm.}$$

where θ is the grazing angle of incidence.

The X-rays came from tubes of the Coolidge type. One of the t had a tungsten target and the other had a rhodium target.

The X-rays passed through two narrow slits before they reached the cite crystal. As the third slit, that in front of the ionization chamber large enough to admit the entire reflected beam, this method elimi large corrections for the penetration of the X-rays into the crystal

The electrical current (2 milliamperes) through the X-ray tube from a high potential storage battery. In most of the experiment held the difference of potential between the electrodes of the tube stant at 37,750 volts, and, if any small unavoidable variation from value occurred, we corrected for it.

In order to avoid actually determining the zero point on the sca the instrument we either measured the lines on each side of it, or found their positions in both the first and the second order spectra. various sets of measurements agree with each other to within the li of experimental error.

In order to determine whether or not the critical absorption frequ differs from the critical ionization frequency, we filled the ioniz chamber with methyl-iodide and used a thin layer of potassium io as the absorber.

The curves in Fig. 1 represent the ionization currents as functio the readings of the verniers attached to the crystal table. The cu A and A' refer to experiments in which no absorber was used. sharp breaks in the curves occur at angles corresponding to the cri ionization wave-length of iodine. X-rays of shorter wave-length this critical wave-length produce more ionization than X-rays of lo wave-length do. Measuring from the center of the drop on one si the zero to the center of the drop on the other side we get for the do grazing angle 2θ (after subtracting an excentricity correction of $2\theta = 7'\ 4'\ 25''$. Whence the critical ionization wave-length $\lambda_i = .3736 \times 10^{-8}$ cm.

Curve B represents an experiment in which the X-rays passed thr

a thin layer of potassium iodide before reaching the spectrometer. The iodine in the salt absorbs X-rays of shorter wave-lengths than the critical absorption wave-lengths to a greater extent than it does longer waves. The magnitude of the change in the absorption depends, of course, upon the thickness of the absorbing layer, and in this experiment the layer was thick enough to more than counteract the increase in ionization for X-rays shorter than the critical ionization wave length. The ordinates in curve *C* are the ratios of those in curve *B* to those in curve *A* respectively. Curve *C* represents, therefore, the true critical absorption effect un-

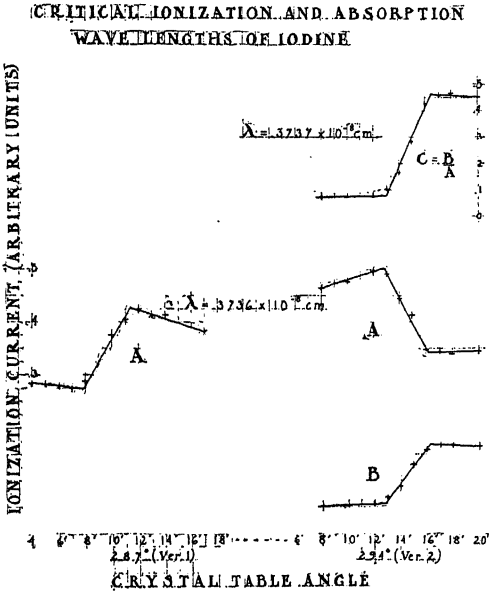


Fig. 1.

influenced by the change in ionization at the critical ionization wave-length; and the angle measured to the center of the drop corresponds to the critical absorption wave-length λ_a. It appears from the graphs that the centers of the drops in curve *A* and curve *C* fall sensibly at the same abscissa; that is, the angles corresponding to the critical absorption and critical ionization wave-length do not differ from each other by more than a few seconds of arc. A difference of 10″ of arc could be detected, which means that *the critical absorption and critical ionization wave-lengths are equal to each other to within less than 1/10 per cent.*

In order to determine whether or not the K critical absorption wave-length (λ_a) of a chemical element is the same as that of the γ emission line in the K series we have investigated the emission spectrum of an

The curves in Fig. 2 represent the ionization currents as functions of the readings of one of the verniers attached to the crystal table.

For the two α lines readings were taken 15″ of arc apart on both sides of the zero. The peaks corresponding to these two lines are separated from each other, but the separation appears to be better on the right hand side than on the left. Some slight inequality in the structure of the crystal planes may account for this.

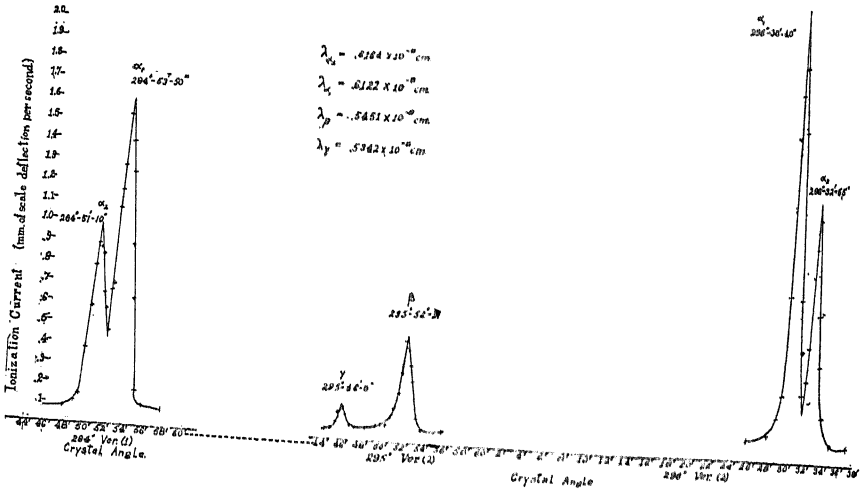


Fig. 2.

As the difference between the wave-lengths of the two α lines amounts to only two thirds of one per cent. this gives an idea of the precision with which the wave-lengths can be estimated. It appears to be possible to determine between which two settings of the instrument a peak lies, and also which of the two settings it lies nearer to. This means that the precision of the measurement is the precision with which the angles can be read by means of the verniers. The verniers' scales are supposed to give readings to 5″ of arc. By estimating from several readings on the two sides of each peak it seems reasonable to suppose that the wave-lengths can be determined with a precision considerably less than one tenth per cent., the grazing angles for these lines being larger than 6°.

The curves in Fig. 2 show also the peaks corresponding to the β and γ lines. The readings for these were taken on one side of the zero only, but the wave-lengths have been calculated from the zero determined by the α line measurements.

The curves in Fig. 3 represent the two α line peaks in both the first and the second order spectra. Passing from the first to the second order

spectrum the distance between the two peaks about doubles itself, while the breadth of each peak remains about the same.

The wave-lengths of the α lines calculated from the first and second order spectra, without direct reference to the zero, equal the corresponding wave-lengths calculated from the first order spectra alone.

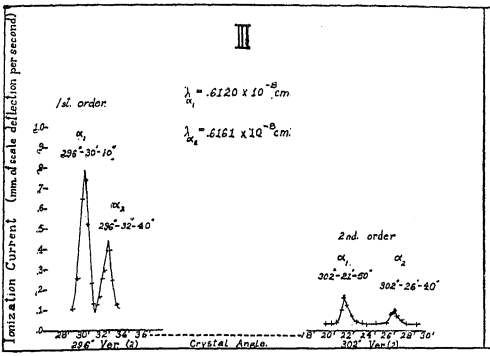


Fig. 3.

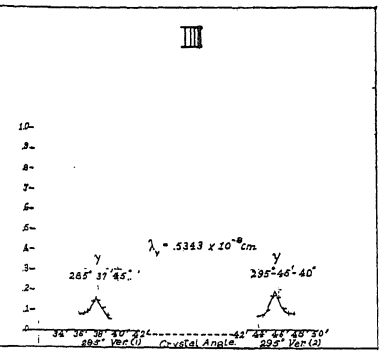


Fig. 4.

The peaks in the curves of Fig. 4 correspond to the γ line in the first order spectrum on each side of the zero.

The curves in Figs. 2, 3 and 4 furnish three independent methods of estimating the position of the zero on the scale.

A correction for eccentricity amounting to about 45″ of arc must be subtracted from the double grazing angle.

The following table contains the wave-lengths of all four lines.

K Series of Rhodium (45). $\lambda \times 10^8$ *cm.*

α_2.	α_1.	β.	γ.
.6164	.6122	.5451	.5342
.6163	.6121	.5453	.5343
.6164	.6120	.5454	.5342

In 1917[1] Prof. F. C. Blake and one of us obtained the value $\lambda = .5324 \times 10^{-8}$ cm. for the critical K absorption frequency of rhodium. As this differs from the values of λ_γ contained in the above table by slightly more than the probable error of the measurement, and as the spectrometer had been partly dismantled and the parts reassembled, the authors of this paper decided to re-measure the critical absorption wave-length.

For this purpose we used the tungsten target X-ray tube and an absorbing layer of rhodium salt placed between the tube and the spec-

Measuring from the centers of the sharp breaks in the curve two sides of the zero line, we get for the critical K absorption wav of rhodium $\lambda = .5330 \times 10^{-8}$. This value agrees with that obt 1917 to within approximately one tenth per cent., but differs f wave-length of the γ emission line by almost one fourth per cen

In order to obtain additional evidence as to whether or not th ence really exists, we have made some experiments using the target tube both with and without the rhodium salt absorber.

The curves in Fig. 5 represent the results obtained. The w

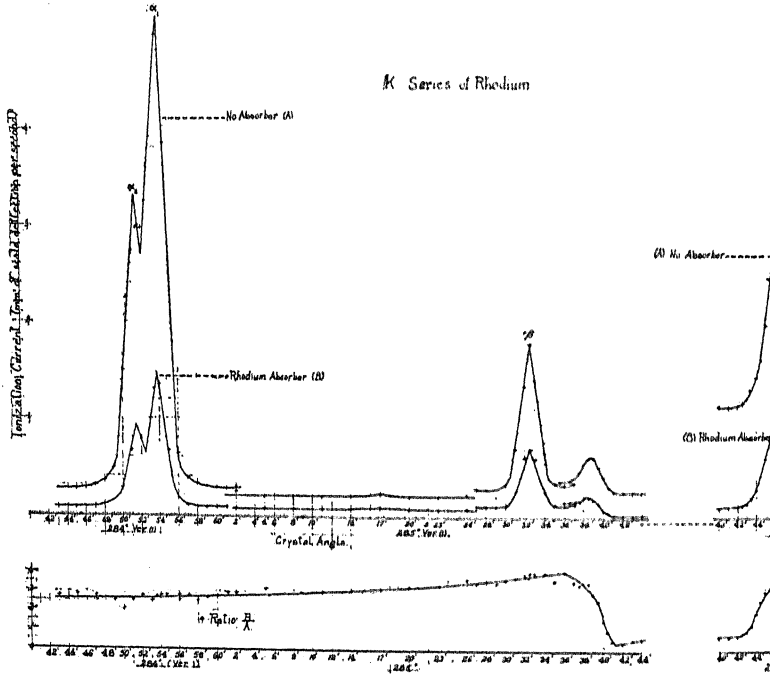


Fig. 5.

the slits were somewhat larger than in the previous experiments were larger, also, for the measurements on the right hand sid zero, than on the left. The readings for corresponding part curves with and without the absorbing screen were made on t day, but the readings for different sections of the curves were different days. This is shown by the discontinuities in and over of the curves.

Curve *A* has been platted from the data obtained without the

ing screen, and curve B, with the absorbing screen. The third curve below represents the ratio of the B to the A ionization currents.

The curves indicate that *the rhodium has no appreciable selective absorption for the X-rays in its own* α_1, α_2 *and* β *emission lines.* The marked increase in absorption occurs, however, close to the peak representing the γ line. Further the wave-length corresponding to the center of the γ line peak is about one third per cent. longer than that corresponding to the center of the absorption drop.

It appears, therefore, from both experiments that, if the wave-length of the emission line corresponds to the center of the peak, and, if the critical absorption wave-length corresponds to the center of the absorption drop, *the critical absorption wave-length is about one fourth per cent. shorter than that of the* γ *emission line.*

Reprinted from the PHYSICAL REVIEW, N.S., Vol. XIV, No. 5, November, 1919.]

ON THE SPECTRUM OF X-RAYS FROM AN ALUMINIUM TARGET.[1]

BY WILLIAM DUANE AND TAKEO SHIMIZU.

SYNOPSIS.

Aluminium Spectrum.—The object of the research has been to investigate the question whether or not the frequencies of the K series are the highest X-rays frequencies characteristic of a chemical element. Several investigators have found experimental evidence, which they interpret as indicating the existence of characteristic emission or absorption of frequency higher than those in the K series. For aluminium the wave-lengths corresponding to these frequencies are stated to be $.37 \times 10^{-8}$ cm. and $.49 \times 10^{-8}$ cm. The authors of this paper have examined the emission spectrum of aluminium between the wave-lengths $.1820 \times 10^{-8}$ cm. and 1.259×10^{-8} cm. Four small peaks appear on the curves, indicating characteristic radiation at wave-lengths $.622 \times 10^{-8}$ cm., $.705 \times 10^{-8}$ cm., $.975 \times 10^{-8}$ cm. and 1.18×10^{-8} cm. The first two belong to the K series of molybdenum, and undoubtedly come from the metallic molybdenum in the Coolidge carthode in the X-ray tube. The last two belong to the L series of lead, and undoubtedly come from the lead screens containing the slits through which the X-rays passed before they reached the X-ray spectrometer.

No other peaks appear on the curve, and this leads to the conclusion that, within the range examined, aluminium has no emission lines the intensities of which amount to as much as 2 per cent. of the general radiation in the neighborhood.

SEVERAL investigators[2] have obtained experimental evidence, which they interpreted as indicating the existence of the emission or the absorption of X-radiation characteristic of a chemical element (the J-series), and of higher frequency than those in its K-series. Barkla and white (*l.c.*) measured the coefficient of absorption of X-rays in copper, aluminium, paper, water, and paraffin-wax. On platting these coefficients against the wave-lengths, and also on platting the coefficients for one substance against those for another (copper) certain breaks in the curves appeared, similar to, but very much smaller than the breaks that occur at the critical absorption wave-lengths associated with the K and L series of characteristic X-rays. From these breaks they inferred the existence of X-radiation characteristic of aluminium, oxygen and carbon at the wave-lengths $.37 \times 10^{-8}$ cm., 39×10^{-8} cm. and $.42 \times 10^{-8}$

[1] A paper read at the New York meeting of the American Physical Society, March 1, 1919.

[2] C. G. Barkla, Roy. Soc. Phil. Trans., 217, pp. 315–360, Aug. 29, 1917. C. G. Barkla and Margaret P. White, Phil. Mag., 34, pp. 270–285, Oct., 1917. C. M. Williams, Roy. Soc. Proc., 94, pp. 567–575, Aug. 1, 1918.

Curves AB and $A'B'$ represent an experiment in which the diff of potential applied to the tube amounted to about 53,200 volts. points A and A', where the curves begin to rise above the natural i tion leak of the instrument, correspond to the frequency which, multiplied by Planck's action constant, h, equals the energy acc by an electron in the X-ray tube as given by the product of the diffe of potential into its electric charge.[1]

The position of the zero on the scale was estimated from these points A and A'. A correction of 45″ of arc must be subtracted the double grazing angle of incidence 2θ on account of the scale's e tricity, when calculating the wave-lengths from the usual for $\lambda = 6.056 \times \sin\theta \times 10^{-8}$ cm.

At the points marked C and C' occur sharp breaks in the cu These are due to the fact that the ionization chamber contained me iodide. The critical ionization wave-length of iodine is $.3737 \times 10^{-8}$ and X-rays of shorter wave-length than this ionize the gas much r strongly than X-rays of longer wave-length do.

As the break in the absorption curve obtained by Barkla and W (*l.c.*), from which they inferred the existence of characteristic J radia occurs at wave-length $.37 \times 10^{-8}$ cm., and as the break in our curve a might completely mask a peak representing characteristic emission li we repeated our measurements over wave-lengths in this neighborh using ethyl bromide in the ionization chamber instead of methyl iodi The curve DE represents this experiment, and no peak appears in that can be interpreted as indicating characteristic emission lines.

Further no peak appears on th curve AB in the neighborhood wave-length $.49 \times 10^{-8}$ cm. at which Williams (*l.c.*) found a break in t absorption curve.

There are, however, two small peaks at wave-lengths $.6219 \times 10^{-8}$ c and $.7051 \times 10^{-8}$ cm. Within the limits of experimental error these a the wave-lengths of the β and α lines in the K series of molybdenu and it is reasonable to suppose that these peaks are due to the presen of the metallic molybdenum in the Coolidge cathode. It is uncerta whether they are to be ascribed to primary radiation from a thin fil of molybdenum deposited on the target during the excessive heatin process to which these X-ray tubes are subjected during their exhaustion or to tertiary, etc., rays excited in the target by secondary rays from th molybdenum in the cathode.

At wave-lengths $.9746 \times 10^{-8}$ cm. and 1.177×10^{-8} cm. appear tw

[1] Duane & Hunt, PHYS. REV., August, 1915, p. 169.
[2] Duane and Hu, PHYS. REV., June, 1918, p. 491.

more small peaks indicating characteristic radiation. These peaks correspond exactly with the β and α lines in the L series of lead, and, doubtless, are due to secondary rays from the lead blocks containing the slits through which the X-rays passed before they reached the spectrometer.

In order to extend the research to X-rays of shorter wave-length than those produced by a difference of potential of 53,200 volts, we took a series of readings with a difference of potential of 71,200 volts. The curve *FG* represents these measurements, and it contains no peak.

Molybdenum and lead are much more efficient radiators of X-rays than aluminium is, for their atomic numbers are higher, 47 and 82 respectively, instead of 13 for aluminium. Further, if the voltage applied to the X-ray tube lies considerably above that required to produce the characteristic rays of its target (as is the case with molybdenum and lead in our experiments), the characteristic radiation is many times more intense than the general radiation in its neighborhood. It is not surprising, therefore, that secondary or tertiary characteristic radiation from molybdenum and lead can produce effects amounting to a few per cent. of the general primary radiation from aluminium, upon which it is superposed, as indicated by our curves.

No peaks representing the emission of characteristic X-rays appear on our curves other than those corresponding to the K series of molybdenum and the L series of lead, and we conclude, therefore, that aluminium has no characteristic lines in its emission spectrum, between the wave-lengths $.1820 \times 10^{-8}$ cm. and 1.259×10^{-8} cm. that amount to as much as 2 per cent. of the general radiation in the neighborhood and that can be produced by the voltages we employed.

HARVARD UNIVERSITY.

[Reprinted from the PHYSICAL REVIEW, N.S., Vol. XIV, No. 6, December 1919.]

ON THE X-RAY ABSORPTION FREQUENCIES CHARACTERISTIC OF THE CHEMICAL ELEMENTS.

BY WILLIAM DUANE AND KANG-FUH-HU.

SYNOPSIS.

Object.—The object of this paper is to record in some detail the data presented to the American Physical Society at its meeting on April 27, 1918.[1]

Blake and Duane[2] had determined the critical absorption wave-lengths associated with the K series of x-rays for most of the chemical elements from bromine (atomic number 35) to cerium (atomic number 58) by measuring the currents in an ionization chamber attached to an x-ray spectrometer. The research reported in this paper extends the measurements to chemical elements of lower atomic number, as far as manganese (atomic number 25). The same apparatus was used as in the previous research, except that the x-ray tube employed had a long glass tube attached to it carrying a thin glass window at its end. This window lay close to the spectrometer slit, and the device materially reduced the absorption of the long x-rays by the air and glass.

Importance in Theory.—These critical absorption wave-lengths have considerable importance in connection with the theories of the structure of matter and the mechanism of radiation, for they represent frequencies of vibration that are the highest x-ray frequencies definitely known to be characteristic of the chemical elements.

Results.—From the experiments it appears that the square root of the critical absorpion frequency is not quite a linear function of the atomic number.

If we calculate the velocity v of an electron in the x-ray tube required to produce the radiation from the equation

$$\frac{1}{2}\frac{m_0 v^2}{\sqrt{1-\frac{v^2}{c^2}}} = h\nu \qquad (1)$$

using for ν the critical absorption frequency, we find that v is a linear function of N, namely

$$v = v_0\,(N - 3/2),\ v_0 = .00678xc \qquad (2)$$

for all the chemical elements from manganese to cerium.

Further equation (2) gives the critical velocity for the chemical elements as far as magnesium, if we use data obtained from emission spectra.

It will be noticed that equation (1) contains the expression for the *transverse* mass of the electron.

IN Moseley's classical experiments[3] on x-rays he showed that the square roots of the frequencies, ν, of corresponding lines in the characteristic emission spectra of the chemical elements are very nearly linear functions of the atomic number, N, of those elements. Recent researches have confirmed and extended these results. The wave-lengths of about fifteen

[1] PHYS. REV., June, 1918, p. 488.

[2] PHYS. REV., Dec., 1917, 697.

lines in each of the emission spectra of a large number of chemical
have been measured and tabulated. The graphs[1] representing ν
responding lines in these spectra as functions of N are not quite
They bend slightly upward, the curvature becoming more n
the frequency increases.

Attempts have been made to deduce empirical formulas for ν
of N, and some of these,[2] with four arbitrary constants, seem
data very well.

The equations[3] in Bohr's theory of radiation contain the
of the electron. Since m varies with the electron's velocity t
roots of these expressions for the frequencies of rotation and
are not quite linear functions of N. The deviation from the
line law is much the same as that which appears in the graphs rep
experimental data.

It might be expected that the critical absorption frequencies a
with the emission series of x-rays would bear the most fundame
perhaps, the simplest relations to the atomic numbers; for the
to be the most important frequencies characteristic of the che
ments. Their importance rests upon the following facts. (*a*)
absorption frequency equals the critical ionization frequency a
with the same x-ray emission series.[4] The latter probably n
critical frequency for the characteristic emission of electrons wit
energy from the atom. (*b*) The difference between two critica
tion frequencies equals the frequency of one of the emission li
acteristic of the chemical element.[5] (*c*) A critical absorption f
substituted in the quantum equation, $Ve = h\nu$, gives the v
required to produce the emission series associated with it.[6]
critical absorption frequency is the highest x-ray frequency kn
characteristic of its chemical element. It lies very close to, bu
above, the highest frequency in the corresponding emission ser

De Broglie has made a series of interesting and important exp
in which he measured the critical absorption wave-lengths cha
of a large number of chemical elements. He used an x-ray spe
with a rock salt crystal, and determined the position of the
rays reflected from the crystal by means of a photographic pla

[1] Friman, Phil. Mag., Nov., 1916, p. 497.
[2] Uhler, PHYS. REV., April, 1917, p. 325.
[3] Phil. Mag., September, 1913, p. 476.
[4] Duane and Hu, PHYS. REV., June, 1918, p. 489; Dec., 1919.
[5] Duane and Shimizu, PHYS. REV., April, 1919, p. 306; July, 1919.
[6] Webster, PHYS. REV., June, 1916, p. 599; and Duane and Hu, *l.c.*
[7] Duane and Hu, *l.c.*

Owing to the difficulty of estimating by this method the effect due to the penetration of the x-ray into the reflecting crystal, and that due to the widths of the spectrometer's slits, Prof. F. C. Blake and one of us[1] decided to undertake a series of measurements using the ionization method of detecting the reflected beam. The data obtained in these experiments include the critical absorption wave-lengths associated with the K series of x-rays for all but two of the known chemical elements from bromine ($N = 35$) to cerium ($N = 58$).

The equation $\nu = \nu_0 (N - 3.5)^2$, in which ν_0 is the Rydberg fundamental frequency, namely 109,675 multiplied by the velocity of light, approximately represents the critical absorption frequencies ν corresponding to these wave-lengths. There appears to be, however, a small systematic variation from the law represented by the equation.

The object of the research reported in this paper has been to extend the measurements to chemical elements of lower atomic number than that of bromine, and we have succeeded in obtaining the critical absorption wave-lengths associated with the K series for all the chemical elements from bromine ($N = 35$) to manganese ($N = 25$).

The magnitudes of the frequencies belonging to chemical elements having small values of N give us the best determinations of the quantity k in formulas of the general form

$$\nu = \nu_0(N - k).$$

The x-rays in the K series of chemical elements of low atomic numbers are comparatively long; and, since the coefficient of absorption of x-rays varies approximately as the cube of the wave-length, the absorption of the rays of long wave-length by the glass walls of the x-ray tube itself becomes of great importance. In order to allow as much radiation of long wave-length to emerge from the tube as possible we designed, and had constructed an x-ray bulb with a long glass side tube attached to it. This tube extended out toward the x-ray spectrometer, and carried at its end a thin glass window, which lay close to the spectrometer's slit. The device markedly reduced the absorption of the x-rays by the glass and air.

Except for this side tube attached to the x-ray bulb the apparatus used in the experiments on chemical elements from manganese to bromine was exactly the same as that employed in the experiment on chemical elements from bromine to cerium. A detailed description of this apparatus may be found in the PHYSICAL REVIEW for December, 1917, on page 624.

[1] PHYS. REV. December, 1917, p. 607.

The electric current exciting the x ray tube came from a high tension
orage battery containing 20,000 cells, and the voltage across the tube
rminals was kept constant by slowly changing a water resistance in
ies with it. An electrostatic voltmeter, calibrated by means of a
easured current from the storage battery flowing through a known
etallic resistance of 800,000 ohms, served to measure the voltage.
e current through the tube, amounting to several milliamperes was
easured by a milliameter. Two slits in lead blocks placed between the
ay tube and the reflecting crystal defined the beam of rays and the
rd slit, in front of the ionization chamber, was wide enough to allow
the reflected rays to pass. This arrangement eliminates a correction
the penetration of the rays into the crystal. This correction, how
r, is very small for x rays of long wave length.
The absorbing screen consisted of a thin layer of the chemical element,
of one of its salts, and lay between the x ray tube and the first slit.
We made measurements on both sides of the zero line of the spec
meter, and obtained curves for each chemical element representing
e ionization currents as functions of the readings of the verniers
ached to the crystal table, similar to the curves shown on page 701
the PHYSICAL REVIEW for December, 1917. The sharp drops in
se curves correspond to the critical absorption wave lengths, the
gular breadths of the drops representing the effects due to the widths
the slits.
To determine the grazing angles of incidence θ to substitute in the
mula for the wave-length

$$\lambda = 2d \sin\theta \quad \text{to avoid} \quad \sin\theta = n \cdot 10^{-7} \text{ cm},$$

measured from the mid points in the drops. The breadths of the
ps amount to a few minutes of arc, and the grazing angles of incidence
several degrees. The positions of the mid points can be estimated
within 1/10 per cent. of the values of the grazing angles.
The slopes of the curves above and below the drops depend upon the
ing of the instrument, the thickness of the absorbing layer, the
tion between the voltage applied to the x ray tube and that required
produce x-rays as short as the critical rays, etc.
The following Table I. contains the critical absorption data for the
series of all the known chemical elements from manganese ($N = 25$)
cerium ($N = 58$), except the two gases xenon and krypton. The
ical absorption wave-lengths appear in the third column, and the
are roots of the corresponding vibration frequencies, in the fourth.
$\sqrt{\nu}$ cannot quite be represented by a linear function of N. The

TABLE I.[1]

Chemical Element.	Atomic Number.	$\lambda \times 10^8$	$\nu \times 10^{-8}$	Ratio $\beta = v/c$.	$\beta_0 \times 1{,}000$.
[illegible]	[illegible]	[illegible]	3.147	.3828	0.775
[illegible]	[illegible]	[illegible]	3.068	.3761	0.778
[illegible]	[illegible]	[illegible]	3.013	.3698	0.785
[illegible]	[illegible]	.3444	2.983	.3629	0.783
[illegible]	[illegible]	.3375	2.843	.3494	0.784
[illegible]	[illegible]	.3306	2.775	.3426	0.783
[illegible]	41	.3068	2.717	.3358	0.781
[illegible]	[illegible]	.3117	2.659	.3291	0.786
[illegible]	40	.1141	2.601	.3223	0.786
[illegible]	[illegible]	.3032	2.545	.3157	0.790
[illegible]	47	.1850	2.488	.3089	0.789
[illegible]	[illegible]	.2962	2.431	.3023	0.794
[illegible]	[illegible]	.2890	2.373	.2953	0.790
[illegible]	[illegible]	.2824	2.319	.2889	0.797
[illegible]	[illegible]	.2750	2.204	.2751	0.794
[illegible]	[illegible]	.2685	2.149	.2685	0.797
[illegible]	[illegible]	.2627	2.089	.2614	0.791
[illegible]	[illegible]	.2560	2.031	.2547	0.792
[illegible]	[illegible]	.2497	1.974	.2475	0.783
[illegible]	[illegible]	.2443	1.919	.2408	0.784
[illegible]	[illegible]	.2379	1.808	.2272	0.783
[illegible]	[illegible]	.2320	1.751	.2202	0.775
[illegible]	[illegible]	1.0134	1.696	.2135	0.776
[illegible]	[illegible]	1.1116	1.639	.2067	0.780
[illegible]	[illegible]	1.1902	1.590	.2002	0.785
[illegible]	[illegible]	1.2963	1.521	.1922	0.759
[illegible]	[illegible]	1.3784	1.473	.1863	0.774
[illegible]	[illegible]	1.4891	1.420	.1793	0.766
[illegible]	[illegible]	1.6015	1.369	.1730	0.784
[illegible]	[illegible]	1.7096	1.313	.1661	0.780
[illegible]	[illegible]	1.8903	1.260	.1595	0.787

It is interesting to inquire whether some other quantity connected with x radiation may not be a linear function of N. If we calculate the velocity of the electron in the x ray tube required to produce the K emission series from the quantum equation,

$$\tfrac{1}{2}mv^2 = h\nu, \tag{1}$$

assuming that m varies with the velocity according to the law

$$m = \frac{m_0}{\sqrt{1 - \beta^2}}, \qquad \beta = \frac{v}{c}, \tag{2}$$

where c is the velocity of light, we find that the values of v do not differ

[1] We wish to express our sincere thanks to Professor C. James and to Professor J. L. Howe for sending us some of the rare elements.

from those given by the linear equation

$$v = v_0(N - \ldots), \qquad v_0 = \ldots \qquad (3)$$

by as much as 1/5 per cent.

The fifth column in the table contains the values of λ_0 and the sixth, of $\beta_0 = v_0/c$. None of the values of λ_0 differ from ... by as much as 1/5 per cent., except that for zinc.

We have shown by experiment (...) that the critical absorption frequency of rhodium does not differ from the highest frequency in its K emission series by more than about 1/4 per cent. If we calculate the critical velocity v from equations (1) and (2) using for ν the highest frequencies given in Siegbahn's tables of emission lines in the K series, we find that equation (3) represents the velocities with considerable precision for all the chemical elements as far down as and including magnesium ($N = 12$).

The following table contains the data for these chemical elements:

Chemical Element.	Atomic Number.	$\lambda \times 10^3$.	$\nu \times 10^{-8}$.	Ratio $\beta = \ldots$	$\beta_0 = v_0/c$.
Chromium	24	2.067	1.503	1.536	0.282
Titanium	22	2.490	1.097	1.391	0.258
Calcium	20	3.072	.9850	1.253	0.234
Potassium	19	3.446	.9137	1.163	0.231
Chlorine	17	4.391	.8268	1.050	0.234
Sulphur	16	5.014	.7734	0.9839	0.239
Phosphorus	15	5.804	.7188	0.9147	0.268
Silicon	14	6.755	.6664	0.8478	0.238
Aluminum	13	7.982	.6141	0.7812	0.238
Magnesium	12	9.471	.5627	0.7158	0.847

In conclusion we wish to call attention to the fact that $\frac{1}{2}mv^2$ is not the *relativity* expression for the kinetic energy of the electron. The fact that equation (2) gives the *transverse* mass of the electron suggests that possibly v may represent the velocity of an electron travelling in an orbit. These points will be discussed in another paper.

ON THE X RAY ABSORPTION FREQUENCIES CHARACTERISTIC OF THE CHEMICAL ELEMENTS.[1]

By William Duane and Fabio Hunt.

Abstract.

Several researches have been published describing measurements of the critical absorption wave lengths associated with the K series of x rays characteristic of all but two of the known chemical elements from manganese (atomic number $N = 25$) to cerium ($N = 58$). The object of the experiments described in this paper was to extend the measurements to chemical elements of higher atomic number, using the x ray spectrometer.

In the earlier experiments the electric current through the x ray tube was furnished by storage batteries of 20,000 cells, giving an electromotive force of 40,000 volts when fully charged. A difference of potential of 43,000 volts was sufficient to excite x rays of greater frequency than the critical absorption wave-length of cerium, and to make the measurements for those chemical elements having shorter critical absorption wave-lengths, it was necessary to have a higher voltage applied to the x ray tube. The authors, therefore, constructed a transformer with a set of condensers and kenotrons attached to it, by means of which a constant difference of potential of 50,000 volts was obtained. Except for this change in the apparatus, the method of measurement was the same as that used in the earlier researches.

The critical absorption wave lengths were measured for eight of the chemical elements from tungsten ($N = 100$) to lead ($N = 82$) both inclusive. The values of the absorption frequencies corresponding to these wave lengths, when plotted against the atomic numbers, indicate a still greater departure from the straight line relation than do the values previously obtained for elements of lower atomic number.

As has been shown, [2] the equation

$$\nu = \frac{2\pi^2 e^2 m}{h^2}(N - \sigma)^2 \qquad (1)$$

represents the relation between the velocity of the electrons in the x ray tube required to excite the characteristic emission series of a chemical element of atomic number N, and that element's absorption frequency ν. The values of ν calculated by the quantum relation, using the experimentally determined values of V, agree with those calculated by the same formula for elements of atomic numbers higher than 58 fall slightly below those given by equation (1). The greatest variation from the equation amount to a little over 1 per cent.

SEVERAL papers have been published[2] describing measurements of the critical absorption wave lengths associated with the K series of x rays characteristic of all but two of the known chemical elements from manganese (atomic number $N = 25$) to cerium ($N = 58$) both inclusive.

[1] A paper presented at the Baltimore meeting of the American Physical Society, December 28, 1918.

[2] Hjalmar and Duane, Phys. Rev., Dec., 1917, p. 697; and Duane and Hu, Phys. Rev., June, 1918, p. 488.

In these experiments the electric current flowing through the x-ray tube came from a storage battery of 20,000 cells, giving, when fully charged, a difference of potential of about 45,000 volts. This difference of potential can not produce x-rays much shorter than the K critical absorption wave-length of cerium, and, as the critical wave-length decreases quite rapidly with increasing atomic number, it was found impossible to make good measurements for elements of higher atomic numbers than 58.

The authors therefore set up a generating plant similar to that designed by Dr. A. W. Hull. This consisted of a high tension transformer attached to a system of condensers and kenotrons for maintaining the voltage approximately constant. The plant gave us voltages up to about 115,000 volts and we were able to measure the critical absorption wave-lengths associated with the K series of eight of the chemical elements, from neodymium ($N = 60$) to lead ($N = 82$).

Except for the generating plant the apparatus did not differ from that used in the earlier researches [*l. c.*], and the same precautions were taken to eliminate errors due to the penetration of the x-rays into the reflecting crystal (calcite), and to the width of the spectrometer's slit.

Curves were drawn for each chemical element similar to those published on page 701 of the PHYSICAL REVIEW for December, 1915, and the angular distances between the mid points in the characteristic gave us the grazing angle of incidence, θ, from which to calculate the wave lengths by the formula

$$\lambda = 0.4058 \times \sin\theta \times 10^{-8} \text{ cm}$$

The following table contains the data. The critical absorption wave-lengths appear in the third column, and the square roots of the corresponding vibration frequencies in the fourth.

The values of the critical absorption wave lengths given by de Broglie are several per cent. smaller than ours.

Chemical Element.	Atomic Numbers	$\lambda \times 10^8$	$\nu^{\frac{1}{2}} \times 10^{-4}$	Ratios	$\Delta\nu^{\frac{1}{2}} \times 10^{-4}$
Neodymium	60	2861	4.242		0.234
Terbium	65	2398	4.646	1.095	0.243
Dysprosium	66	2308	4.694	1.106	0.253
Tungsten	74	1786	5.092	1.200	0.276
Osmium	76	1684	5.253	1.238	0.284

On plotting the square roots of the vibration frequencies against the atomic numbers it can be seen that they depart from the straight line law still further than do the values previously obtained for chemical elements of lower atomic number.

It has been shown[2] that the velocity of the electrons in the x-ray tube required to produce the K emission series obeys the law represented by the equation

$$\beta = \frac{v}{c} = \beta_0 - 0.0007830(N - 3.2), \tag{1}$$

for chemical elements up to cerium ($N = 58$), provided that we calculate v from the quantum equation,

$$\tfrac{1}{2}mv^2 = h\nu. \tag{2}$$

In this equation $\nu = \nu_0$ is the critical absorption frequency, and m, the transverse mass of the electron, is given by the equation

$$m = \frac{m_0}{\sqrt{1 - \beta^2}}. \tag{3}$$

The fifth column in the table contains the values of $\beta = v/c$ calculated by equations (2) and (3), putting $h = 6.555 \times 10^{-27}$, $m_0 = 8.089 \times 10^{-28}$ and $c = 2.99796 \times 10^{10}$.

In the sixth column appear the values of β_0 calculated from the expression $\beta = N - 3.2$. The differences between these values of β_0 and that found previously for chemical elements of lower atomic numbers, namely, 0.000783, increase progressively with increasing atomic number, N, the greatest difference being a little more than 1 per cent.

As suggested in a former paper the fact that the *transverse* mass of the electron enters into the equations may mean that v is really the velocity of the electrons in an orbit. If so, the above variation in the value of β_0 may be due to the magnetic effect of the electrons in a ring on each other, and not to a lack of constancy in their angular momenta.

Harvard University

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THE RELATION BETWEEN THE INTENSITY OF GENERAL X RADIATION AND THE ATOMIC NUMBER OF THE ANTICATHODE.[1]

By William Duane and Takeo Shimizu.

SYNOPSIS.

Object. The intensity of general x radiation is known to be approximately proportional to the atomic weight of the element constituting the anticathode, provided the other conditions are the same. But since the atomic weights are, roughly speaking, proportional to the atomic numbers, it may be that the intensity is proportional to the latter instead of the former, considering the important part which the atomic number plays in the phenomena of characteristic x radiation. The object of the present experiment was to decide this point.

Experiment. We used the four successive elements iron, cobalt, nickel and copper because of the advantage that the atomic weights of cobalt and nickel are in the reverse order to their atomic numbers. An x ray tube of special type, which could be used successively with each of the four elements in the form of a Coolidge cathode without changing the geometrical relations between the focused point and the measuring apparatus, was excited by a large storage battery of available voltage up to 40,000. The intensity of the rays coming out of the tube, which were almost free from characteristic radiation, was measured by means of an ionization chamber and electrometer.

Result. The intensity was found to be proportional to the atomic number and not to the atomic weight for the above four elements. This was particularly clear because the observed intensities for cobalt and nickel were in the reversed order of their atomic weights.

THE total intensity of general x radiation regarded as a function of the velocity of the exciting electrons and also as that of the chemical nature of the anticathode was first treated theoretically by J. J. Thomson[2] in 1907. His conclusion, based upon certain assumptions, was that the total intensity should be (I.) proportional to the fourth power of the velocity of the exciting electrons and (II.) independent of the chemical constitution of the anticathode. The first part of the conclusion was a mere anticipation at that time, but it was proved to be true by later experiments of other investigators, especially those of Beatty,[3] who showed that the above law was valid for the general x-radiation. The

[1] A paper presented at a meeting of the American Physical Society, April, 27, 1918.

[2] J. J. Thomson, Theoretical Origin of Radiation from Hot Bodies, Phil. Mag., 14, pp. 232–233, Aug., 1907.

[3] R. Beatty, Intensity of Röntgen Rays, Roy. Soc., Proc., Ser. A, 80, pp. 314–327.

second part was, however [illegible] that the heavy metals are more [illegible] other ones. Thomson attributed the [illegible] theory and the fact to the effect of [illegible]

The first systematic [illegible] intensity of general radiation and the [illegible] was made by Kaye[1] in 1908. He showed that the [illegible] proportional to the atomic weight of the [illegible] metals he used. This relation was also [illegible] experiment of Beatty *l. c.*).

The work of Moseley on the [illegible] showed the great importance of the [illegible] nuclear phenomena, and the question arose [illegible] intensity is proportional to the atomic weights of the [illegible] as shown by Kaye and others, or to their atomic numbers. Since the atomic numbers are nearly proportional to the atomic weights the answer could not be given without making experiments specially for [illegible] object of the present investigation is to settle this question.

There are three sets of successive elements in the order of [illegible] the atomic weights and the atomic numbers of which are in the reversed order. For these elements the parallelism between the two quantities is broken, so that they may advantageously be employed in our present inquiry. One of those pairs is that of nickel and cobalt the atomic weights of which are 58·68 and 58·97 and the atomic numbers 28 and 27 respectively. It is to be noticed that there existed a controversy about the atomic weights of these elements before the important rôle of atomic number was pointed out by Moseley. Thus Barkla and Sadler[2] proposed in 1907 that the atomic weight of nickel might be higher than that of cobalt, despite the fact that the reverse is considered to be established in chemistry. They based their argument upon the penetrating power of secondary X rays radiated from different elements. At about the same time, J. J. Thomson[3] observing the intensity of secondary rays from various elements exposed to X rays obtained the results which harmonized with the above view. On the other hand, Hackett[4] found that the intensities of secondary rays from these metals

[1] C. W. C. Kaye, Röntgen Rays. [illegible] Proc. Roy. Soc. A, 209, pp. 123–132, Nov. 23, 1908.

[2] C. G. Barkla and C. A. Sadler, [illegible] Phil. Mag. 14, pp. 408–422, Sept., 1907.

[3] J. J. Thomson, Secondary Röntgen Radiation. [illegible] Phil. Mag. 15, pp. 99–109, 114, March 6, 1908.

[4] F. Hackett, [illegible]

exposed to the β rays of radium were in the same order as their atomic weights, and was opposed to Barkla and Sadler's proposition.

In the present experiment we have measured the intensity of general x radiation from the four successive elements iron, cobalt, nickel, and copper. In order that the x rays from all four metals should pass through exactly the same thickness of glass and follow the same path in space, the x ray bulb indicated in the figure has been used.

Four similar plates of quadrant shape, one of each of the four metals, were soldered to a circular block of copper A, which served as anticathode. The surface consisting of the different metals was carefully turned in a lathe, so that the entire surface made a good plane perpendicular to the axis of a circular copper rod R, which was rigidly attached to A. This rod R could rotate in two copper bearings BB fixed to the glass wall of the tube, but could not slip in the direction of its length. A small piece

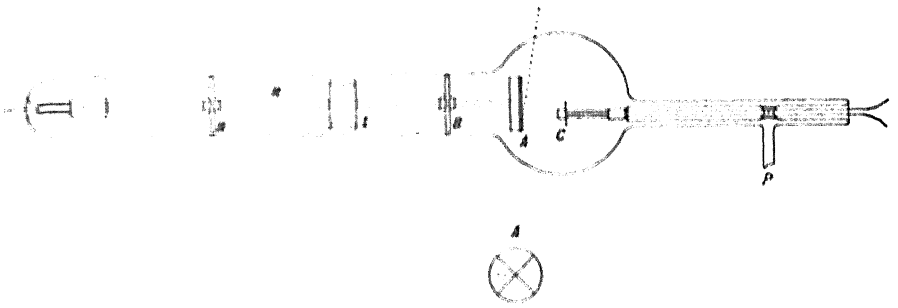


Fig. 1.

of soft iron I, fastened to R made it possible to rotate the anticathode from outside of the tube with an electromagnet.

A Coolidge cathode C was fastened to the tube a little excentric with the axis of R, so that when A was turned around its axis to a suitable position, the cathode rays from it might strike A at the middle of any desired one of the four quadrants, as indicated in the lower figure by a dotted circle.

The side tube P was connected to a Langmuir diffusion pump and a pressure gauge.

As the source of high potential, we employed the 42,000-volt storage battery belonging to the laboratory. The potential across the tube was taken from a suitable number of its sections, and carefully kept constant during observation by adjusting a water rheostat connected in series with the tube. A sensitive static voltmeter made it easy to detect a

through the bulb was also kept constant by adjusting the heating current of the cathode filament.

The x-rays coming out of the bulb sustaining a small angle with the surface, as indicated by a dotted line in the figure were measured by means of an ionization chamber containing saturated vapour of methyl iodide and a Wilson tilted electroscope. Two lead slits placed between the bulb and the ionization chamber defined the solid angle of the measured x-rays. To secure a good constancy of the geometrical relations, the bulb was set up at a distance of about one meter from the nearer slit.

Our object being to compare the radiation from the four metals with one another, observations were taken for them in immediate succession at a constant voltage. But a repetition of one particular observation after an interval of about a month gave almost the same result as was obtained before, indicating that the geometrical relations between the different parts remained unchanged during that time.

A simple calculation showed that the characteristic rays from the metals were almost completely absorbed by the walls of the bulb, so that the observed intensity was due to the general radiation only for all of the metals. The table contains the observed result.

Volts.	Ionization Current · Volts per Sec.			
	Cu (29).	Ni (28).	Co (27).	Fe (26).
19,140	.0218	.0240	.0252	.0220
21,430	.0386	.0428	.0444	.0416
24,120	.0544	.0582	.0602	.0562
27,300	.0812	.0890	.0902	.0842
30,110	.1088	.1061	.1021	.0984
32,400	.1327	.1298	.1351	.1230
40,870	.238	.241	.254	.214

Volts.	Relative Intensity, Fe = 1.00 Calculated from the Above.			
	Cu.	Ni.	Co	Fe.
19,140	1.127	1.091	1.043	1.000
21,430	1.149	1.116	1.028	1.000
24,120	1.106	1.081	1.020	1.000
27,300	1.109	1.079	1.041	1.000
30,110	1.109	1.082	1.041	1.000
32,400	1.097	1.070	1.034	1.000
40,870	1.110	1.079	1.042	1.000
Mean.....	1.115	1.085	1.044	1.000
Ratio of atomic nos.	1.115	1.077	1.038	1.000

Thus we see that the ratios of the intensities of the general x-radiation produced at the same potential by the different metals are independent of the potential within the limits of errors, at least for the voltages used, and that the intensities are very nearly proportional to the atomic numbers of the elements. This is particularly evident in this case since the order of the atomic weights is not the same as that of the atomic numbers. The intensity follows the order of the atomic numbers and not that of atomic weights.

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ON THE K SERIES OF X-RAYS

By William Duane and Wilhelm Stenström

Jefferson Physical Laboratory, Harvard University

Communicated July 1, 1920

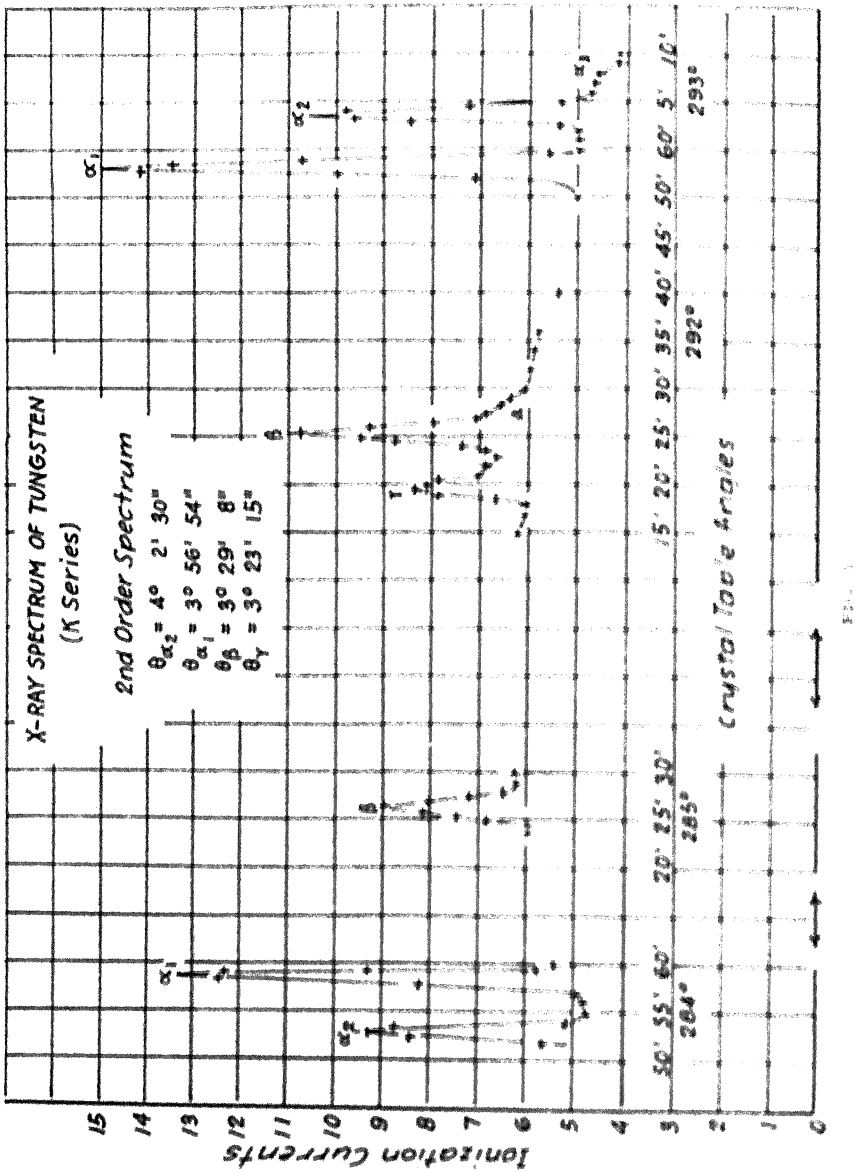
In the research reported in this paper the authors have measured the wave-lengths of the emission lines and that of the critical absorption in the K series of tungsten. In order to obtain as precise values of the wave-lengths as possible they employed spectra of the first, second, third, fourth and, in one instance, the fifth order.

The object of the research has been to provide data for testing the following points: (*a*) The existence of a third line in the α-group; (*b*) the separation of the critical absorption from the line of shortest wave-length in the emission spectrum, namely the γ line; (*c*) the experimental and theoretical relations between the various lines in the K, L_{III}, M, etc., series; (*d*) the relative intensities of the emission lines; and (*e*) the equations for the wave-lengths that may be deduced from theories of the structure of atoms and the mechanism of radiation.

The X-ray spectrometer, the generating plant used to operate the X-ray tube, the instruments for controlling the current and voltage and the

Physical Review. The chief difference between this and previous researches lies in fact that we have used spectra of higher orders, thus obtaining greater dispersion and precision.

Measurements of the electric current in the ionization chamber of the



spectrometer were made at intervals of 30" of arc on the scale which gives the grazing angle of incidence of the X rays that strike the crystal. The

The tips of the peaks in these curves correspond to the lines in the characteristic X ray spectra. It is possible to determine with certainty between which two settings of the crystal a peak lies, and also about how far from each it is. This means that, when the apparatus is functioning well, the grazing angle of incidence can be estimated to within about 7″

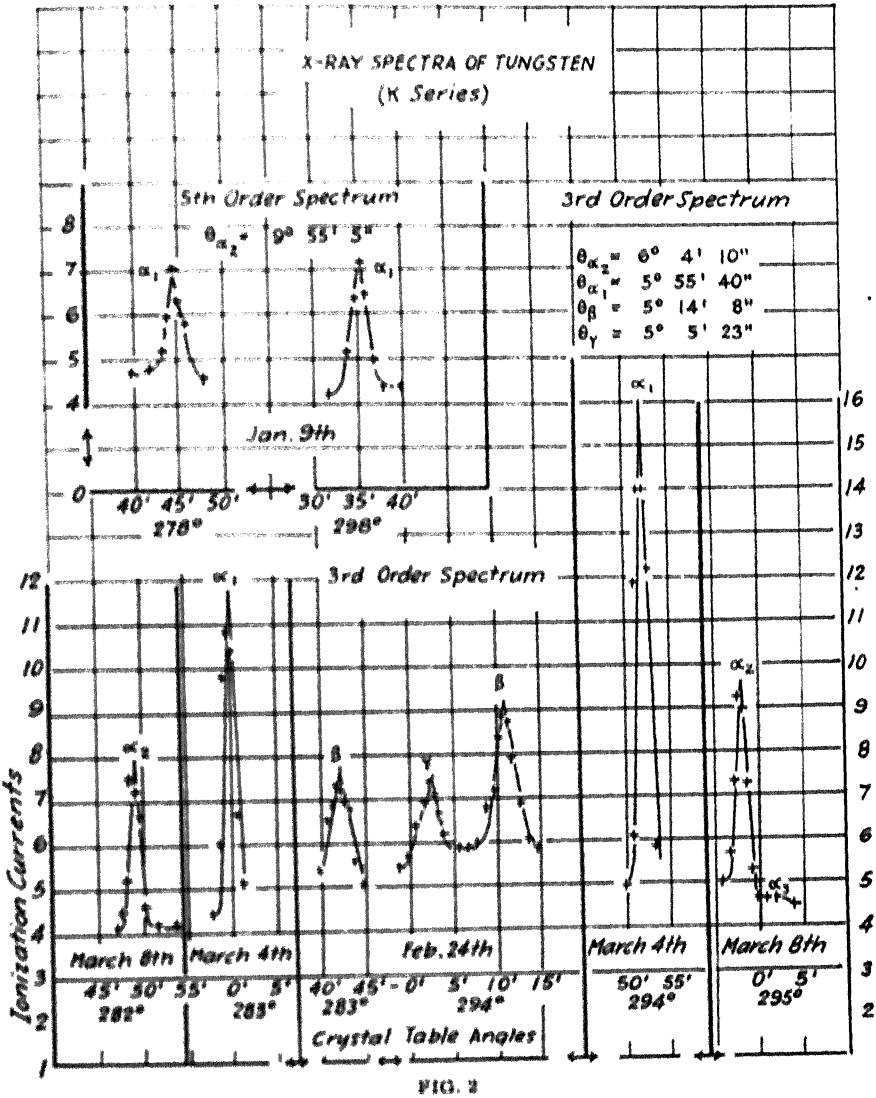


FIG. 2

of arc. For the tungsten K series the grazing angles of incidence in the first order spectrum amount to about 2° = 7200″, and, therefore, the error in a satisfactory determination of a wave-length ought not to ex-

In estimating the wave lengths, etc., only those measurements may be used that are made on the same date, for the zero of the instrument may have shifted between the dates recorded in the figures.

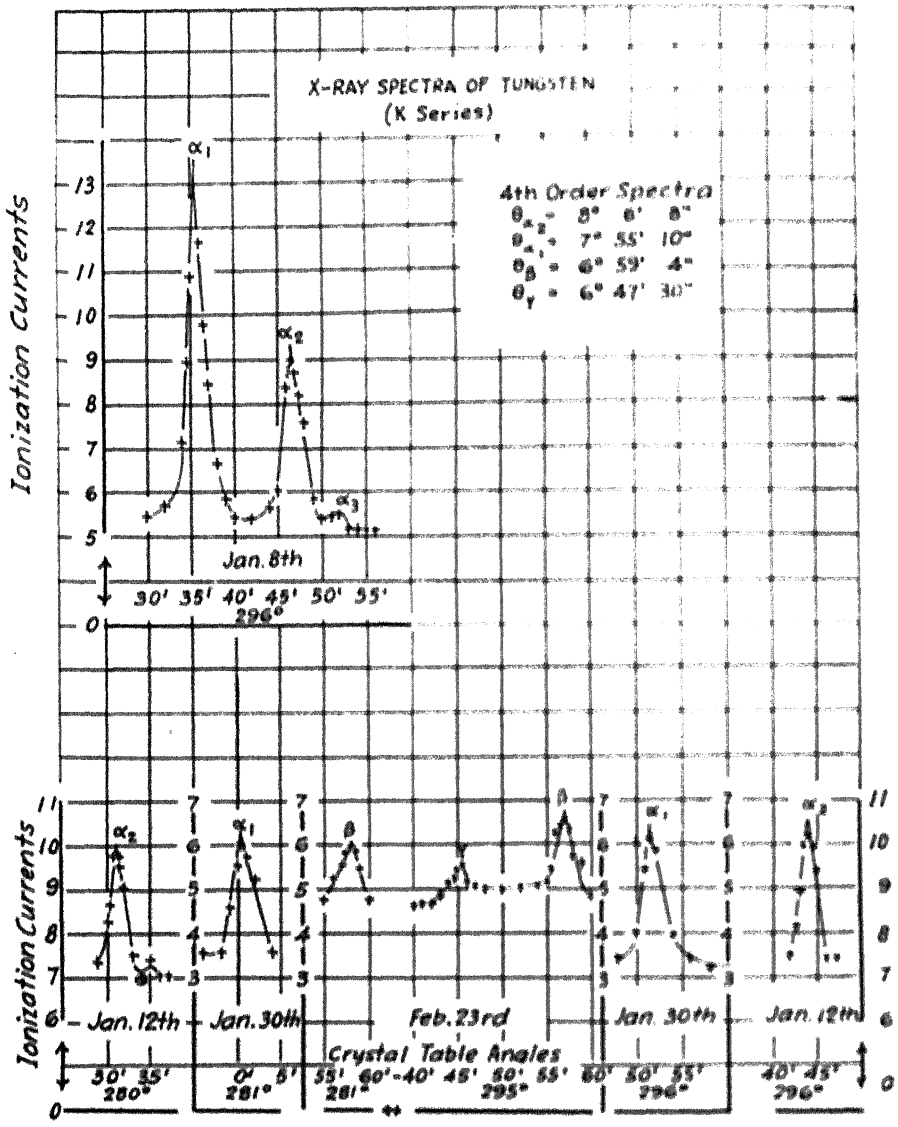


FIG. 3

The following table contains the wave-lengths, λ, calculated from the average grazing angles of incidence, θ, obtained from all the measurements we have made in the spectra of the various orders, respectively

TABLE 1

K SERIES OF TUNGSTEN

$n\lambda = 0.1005 \times \sin\theta \times 10^{-8}$ cm.

LINE NUMBER OF SPECTRUM	$\lambda \times 10^{8}$ cm					
	α_3	α_2	α_1	β	γ	ABSORPTION
1				0.18441	0.17898	0.17833
2		0.21342	0.20850	0.18415	0.17880	0.17810
3		0.21339	0.20848	0.18420	0.17909	0.17795
4	0.215	0.21341	0.20862	0.18418	0.17905	
5			0.20862			
Weighted Means	0.215 ± 10	0.21341 ± 3	0.20860 ± 4	0.18420 ± 3	0.17901 ± 6	0.17806 ± 7
Last Year		0.2131	0.2087	0.1842		0.1785
Siegbahn		0.21345	0.20878	0.18430	0.17934	
$\frac{1}{\lambda}$	1.65	1.68858	1.79938	5.4290	5.58633	5.6160
ν	1230	1250.3	1368.7	4947.4	5090.9	5118.0
$\frac{\nu}{\nu_R}$						

The seventh line in the table contains the weighted mean values of the wave lengths, together with a rough estimate of the precision of the measurements. The γ wave length is more difficult to measure than the others owing to the fact that the critical absorption wave-length lies so near it. The target of the X ray tube absorbs some of its own rays.

In order to estimate the absolute accuracy of the wave-lengths we must, of course, as in all work in X ray spectra, take account of the errors in the grating constant of the reflecting crystal. These appear to add up to about 0.0003_{n}. (See a "Report on Data Relating to X-Ray Spectra," published by the National Research Council.)

For purposes of comparison we have added, in the eighth and ninth lines, respectively, the values obtained last year by the ionization method (*Physical Review*, July, 1919, p. 67) and those given by Siegbahn (*Phil. Mag.*, Nov., 1919, p. 639), which he measured by photographic methods. A small correction (Γ_{200}) has been made in these wave-lengths corresponding to the value of the grating constant of calcite we use.

In order to test general relations between the wave-lengths and also theoretical equations it is convenient to have at hand the wave numbers, $1/\lambda$, and the ratios, ν/ν_R, of the frequencies, ν, to the fundamental Rydberg frequency, ν_R. In calculating these ratios we have used the Rydberg fundamental wave number, $\nu_R = 109737$, calculated for heavy atoms from the data obtained by Paschen in the spectra of hydrogen and helium. Line 10 in table 1 contains the values of $1/\lambda$, each divided by 10^5, and line 11 contains the values of ν/ν_R, calculated from our values of λ.

I. Dr. R. A. Patterson cooperated with us in making the measurements of these wave-lengths. We used an X-ray tube with a molybdenum target in these experiments.

It appears from the data that the wave-length of the γ line and that of the critical absorption differ from each other by about [illegible] of 1%. In the K series spectrum of thorium (see *Physical Review*, vol. [illegible], July, p. 369) the two wave-lengths differ from each other by about 1%. If we adopt the theory of electrons revolving in atomic orbits we can explain this difference in wave-length as follows. According to the theory the critical absorption frequency equals the amount of energy required to carry an electron from the K orbit out to the periphery of the atom divided by Planck's constant, h. The γ line is due to electrons falling into the vacancies in the K orbit from orbits outside of those that we may class together and call the M orbits. The amount of energy set free and radiated during one of these transfers of an electron is less than the amount of energy required to lift the electron all the way from the K orbit to the periphery of the atom. Since the frequency of the X-ray emitted during the transfer equals this energy divided by h, it follows that the frequency must be less than that of the critical absorption, and, therefore, its wave-length greater than that of the critical absorption. The γ line is probably complex, and the wave-length we measure must be a kind of centre of gravity of the wave-lengths of its components.

In the second order spectrum (fig. 1) a drop occurs in the curve at a certain point marked "a." This does not belong to the K series of tungsten. It represents the critical ionization of iodine in the first order spectrum, the wave-length of which is $0.3\,3\,3' \times 10^{-8}$ cm. We used methyliodide in the ionization chamber of the spectrometer.

In a research described in the *Physical Review* for July, 1919, p. 67, Mr. Shimizu and one of us obtained experimental evidence showing that the difference between the K critical absorption frequency and any one of the L critical absorption frequencies equals the frequency of one of the emission lines in the K series. Theoretically this relation ought not to be exact, if orbits in some of the atoms are elliptical and in other atoms of the same chemical element, circular. The atoms with elliptical orbits contain amounts of energy that are different from the amounts of energy in atoms with circular orbits, and hence the change in energy when an electron is removed from the K orbit will not be the same in the two cases.[1] This means that the K critical absorption frequency should be complex, and that what we measure is a kind of average frequency. Strictly, according to the theory, the frequency difference law should apply to those atoms only that are exactly alike.

To test this point we have taken the absorption measurements made on the L series of tungsten by Dr. R. A. Patterson and one of us. The law applies, of course, to the wave-numbers as well as to the frequencies.

The wave numbers of the three critical absorptions in the L series of tungsten are

$$La_1 = 0.9281 \pm 1 \quad La_2 = 0.9323 \pm 4 \quad La_3 = 0.9766 \pm 30,$$

each multiplied by 10^8. Subtracting these from the critical absorption wave number in the K series and comparing the differences with the wave-numbers of the three α emission lines we get

		Wave-Numbers, $1/\lambda \times 10^{-8}$	
Ka	$La_1 = 4.792 \pm 0.003$	$K\alpha_1 = 4.7938 \pm 0.001$
Ka	$La_2 = 4.685 \pm 0.003$	$K\alpha_2 = 4.6858 \pm 0.0007$
Ka	$La_3 = 4.639 \pm 0.001$	$K\alpha_3 = 4.65 \pm 0.02$

It appears that in each case the difference between the K critical absorption wave number and one of the L critical absorption wave-numbers equals the wave number of one of the α emission lines to within the limits of error of the measurements. This agrees with the results obtained last year. If the above mentioned effect due to elliptic orbits exists at all, it appears to be too small to detect, with our present methods of measurements, in atoms of as high an atomic number as that of tungsten.

The existence of the third faint line, α_3, and the agreement of its wave-number with the difference between the Ka and La_3 wave-numbers is a point of some theoretical interest. According to Sommerfeld's theory of elliptic orbits the $K\alpha_1$ line is due to the transfer of an electron from the L, orbit to the K orbit, if the L, orbit is circular, and the $K\alpha_2$ line is due to a similar transfer, if the L, orbit is elliptic. The difference between the wave numbers of $K\alpha_1$ and $K\alpha_2$ calculated from the formulas he gives (*Atombau und Spektrallinien*, chapter 5) amounts to 0.1072×10^8, and this agrees very well with our experimental value for the same difference, namely, 0.1080×10^8. There appears to be no explanation on this theory for the third critical absorption, La_3, in the L series, nor for the third line $K\alpha_3$ in the K emission series. It would seem to be necessary to assume that there are at least two L orbits.

The peak corresponding to $K\alpha_3$ seems to be quite well marked on the curves representing spectra of higher order than the first, especially on that representing the fourth order. The line is very faint, having only about $\frac{1}{2}$ % of the intensity of the $K\alpha_1$ line.

The $K\beta$ line is supposed to be due to electrons falling from the M orbit (or orbits) into the K orbit. We can not test the above frequency difference law in this case directly, for the critical absorption frequencies have not been measured in the M series of tungsten. Dr. Stenström, however, has observed three critical absorption wave-lengths in the M series of thorium and uranium. He has measured also the wave-lengths of emission lines in the M series of uranium, thorium and tungsten. Since the relative positions of the critical absorption and certain of the emission

chemical elements, we can estimate approximately where the critical absorption wave lengths lie in the M series of tungsten. Making this estimate, and calculating the three critical absorption wave numbers we obtain the following values, each multiplied by 10^{3}.

$$Ma_1 = 0.152 \quad Ma_2 = 0.157 \quad Ma_3 = 0.185$$

Subtracting these from the K absorption wave number, and comparing the differences with the Kβ emission wave number we get

Ka − Ma_1	= 5.464	
Ka − Ma_2	= 5.459	Kβ = 5.459
Ka − Ma_3	= 5.431	

One of the differences between absorption wave numbers, Ka − Ma_2, lies very close to that of the Kβ line. This suggests that the Kβ line is due chiefly to electrons falling from the third M orbit to the K orbit. If electrons also fell from the second M orbit to the K orbit they would produce a line on the short wave length side of the principle Kβ line. Faint lines on the short wave length sides of the Kβ lines have been observed in the spectra of a few of the chemical elements of low atomic number by Mr. Hjalmar working in Professor Siegbahn's laboratory.[1] The separation of these components of the Kβ line from each other amounts to a small fraction of 1%.

According to Rubinowicz' "Principle of Selection" transfers of electrons from the first M orbit to the K orbit ought not to occur.[2]

The faint component that has been observed by Siegbahn,[1] de Broglie[3] and Hjalmar on the long wave length side of the Kβ line in the spectra of a few of the chemical elements was predicted by Sommerfeld[4] by reasoning from his theory of elliptic orbits.

These components of the Kβ line may account for some of the irregularities in the β peaks on our curves (figs. 2 and 3).

Some years ago Kossel suggested that the difference between the frequencies (or wave numbers) of the Kβ and Ka lines should equal that of a line in the L series. It is well known that this relation, although approximately true, is not quite exact. An explanation for this discrepancy may be found in the supposition that the electrons producing the Kβ line may not come from the same M orbits as those producing the La and Lβ lines.[5] Dr. R. A. Patterson and one of us recently presented to the American Physical Society an account of some experiments which show that the wave-numbers of the $L\alpha_1$, $L\alpha_2$ and Lβ_1 lines of uranium and thorium equal the differences between certain of the L and M critical absorption wave-numbers. These relations may be expressed by the following equations:

$$La_1 = Ma_1 = L\alpha_1, La_1 \qquad Ma_2 = L\alpha_2 \text{ and } La_2 \qquad Ma_3 = L\beta_1.$$

In terms of the transfer of electrons between orbits these equations mean

that the $L\alpha_1$, $L\alpha_2$ and $L\beta_1$ lines are due to electrons falling from the M_1 and M_2 orbits into L orbits, whereas we inferred above that the $K\beta$ line was mainly due to electrons falling from the M_3 orbit into the K orbit. A rough quantitative test for this explanation may be obtained as follows: From the above three equations and the three equations representing the transfers of electrons producing the $K\alpha$ and $K\beta$ lines, namely

$$K\alpha - L\alpha_1 = K\alpha_1, \quad K\alpha - L\alpha_2 = K\alpha_2 \text{ and } K\alpha + Ma_3 = K\beta,$$

we get the equations

$$K\alpha_1 + L\alpha_1 - K\beta - Ma_1 = Ma_1 \text{ and } K\alpha_2 + L\beta_1 - K\beta = Ma_1 + Ma_2.$$

The left hand members of these equations have the values 0.043 and 0.039, respectively, for tungsten. The right-hand members, which are the differences between quantities that we have estimated by extrapolation, have the values 0.030 and 0.025, respectively. These small differences are of the same order of magnitude, which indicates that the explanation is approximately correct. We must remember, however, that the M series is probably more complicated than we have supposed. There are reasons for believing, for instance, that another critical absorption exists, of slightly higher frequency than Ma_1.

The ionization spectrometer furnishes us a method of approximately estimating the relative intensity of the lines in X-ray spectra. At present, however, we are not able to correct for the change with wave-length in the absorption of the rays by the target, the glass walls of the X-ray tube and ionization chamber, the reflecting crystal, etc. Nor do we know exactly how the coefficient of reflection of the crystal varies with the wave-length. It is not safe, therefore, to compare spectral lines that differ very much from each other in wave length.

By estimating the heights of the peaks corresponding to the lines of the K series in the spectra of the first, second, third and fourth orders we have arrived at the following numbers representing approximately their relative intensities:

Line	α_2	α_1	α_1	β	γ
Intensity	4	50	100	35	15

It is interesting to note that, if we apply Sommerfeld's theory of the relative intensity of lines (Atombau und Spektrallinien, chapter 6) to the α_1 and α_2 lines, we get either 3 : 2, or 2 : 1, as the ratio of their intensities. Our experiments favor the latter ratio.

In an address delivered at the St. Louis meeting of the American Association for the Advancement of Science, last December (see *Science*, May 21, 1920, p. 505) one of us presented a set of calculations of the K critical absorption frequencies for a number of chemical elements. The calculations were based on Bohr's theory, with the additional assumption that the electrons were distributed among the orbits in much the same way

as they are distributed in the layers and shells of the Lewis Langmuir static atom. The ratio, ν/ν_∞, of the K critical absorption frequency for tungsten to the Rydberg fundamental frequency is 5.118 according to the theory, which is exactly our experimental value (see table 1). The agreement to four figures between the two values must be regarded as a matter of chance, however, as the errors in both the experimental and calculated numbers amount to a fraction of 1%.

[1] See Sommerfeld's paper on the fine structure of the *A* line *Munchener Akademie*, June 1, 1918 (367)).

[2] Professor Siegbahn kindly communicated these results by letter.

[3] *Physik. Zs.*, **19**, 1918 (441, 465).

[4] *Phil. Mag.*, June, 1919 (601).

[5] *Comptes Rendus*, May 25, 1920 (1245).

[6] *Sitz. Ber. Bayr. Akad. Wiss.*, June, 1918.

[7] Since this explanation was presented to the Physical Society in February, papers by W. Kossel and A. Sommerfeld (*Zeitschrift fur Physik*, Jan., 1920) have reached us. In these papers the same explanation for the discrepancy is discussed as that here put forward.

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CHARACTERISTIC ABSORPTION OF X-RAYS: L SERIES

By William Duane and R. A. Patterson

Department of Physics, Harvard University

Communicated August 2, 1902

Introduction. Critical absorption wave-lengths associated with the L series of X rays have been measured by E. Wagner[1] and M. de Broglie.[2] These scientists have investigated the spectra of ten of the chemical elements from tungsten to uranium, both inclusive. Each employed a photographic X ray spectrometer with a rocksalt crystal. M. de Broglie found two critical absorption wave-lengths characteristic of each chemical element except, in the case of mercury, for which he gives only one. For bismuth, thorium and uranium he found a third, weak band.

In the investigation reported in this note we employed an ionization spectrometer with a calcite crystal. We found three critical absorption wave lengths characteristic of each of the nine elements examined.

A brief discussion of the bearing of this new data on certain empirical laws and on recent theories of the mechanism of X-radiation may be found in the concluding paragraphs.

Apparatus and Method of Measurement. A detailed description of the ionization spectrometer and the method of using it so as to obviate certain errors of measurement has been given in previous articles.[3] These articles also describe the plant for generating and controlling the X-radiation. Two X-ray tubes have been employed, each equipped with a Coolidge cathode and with a thin glass window blown in a side arm. One of these tubes contained a tungsten and the other a molybdenum target. The current exciting the tubes came from a high tension storage battery. The ionization chamber contained ethyl-bromide or methyl-iodide, and sometimes a mixture of both.

In measuring a critical absorption wave-length we place a thin sheet of the chemical element to be investigated (or of a salt containing it) in the path of the beam of rays between the X-ray tube and the first slit of the spectrometer. We then measure the ionization currents for a series of positions of the crystal corresponding to wave-lengths in the neighborhood of the critical values. From these measurements we platt curves representing the ionization current as a function of the crystal table angle (see figs. 1 and 2). At a critical absorption point a sharp drop appears on the curve, indicating that X-rays of shorter wave-length than the critical value are absorbed by the chemical element to a greater extent than X rays of longer wave-length. For the two strongest absorption bands characteristic of each element we have obtained the curves on both sides of the crystal table zero. The angular distance between the mid-points on two corresponding drops gives us twice the glancing angle, θ,

X-RAY ABSORPTION SPECTRA
L SERIES

TABLE
FIG. 1

from which we compute the wave length, λ, by means of the usual formula

$$\lambda = 2d \times \sin\theta,$$

where d is the distance between the reflecting planes of the crystal. The glancing angle for the third and weakest absorption band has been estimated by careful comparison with the neighboring stronger absorption drop obtained in the same series of readings.

Data Obtained. Table 1 contains the results of our measurements. For purposes of comparison we include also the wave-lengths given by Wagner[1] and de Broglie.[2] The angular breadths of the drops vary from

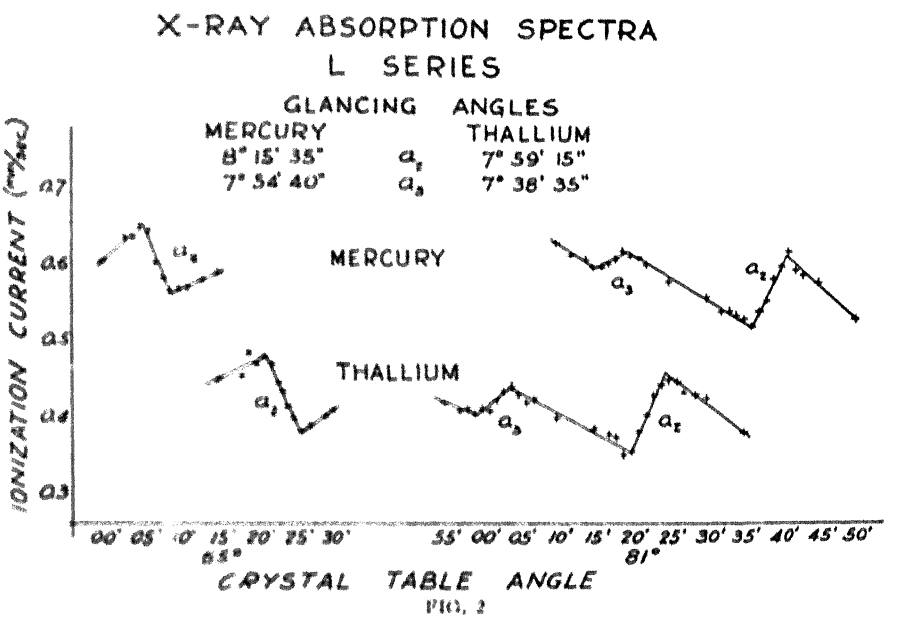


FIG. 2

three to ten minutes of arc according to circumstances, and we believe that we can estimate the positions of their centres to within ten to thirty seconds, depending upon the magnitudes of the drops and the regularity of the curves. Considerations of this kind have given us the estimates of the accuracy of each measurement recorded in the table.

Relative Positions of Emission and Absorption Wave-lengths.—In the article referred to above[3] the authors have called attention to the fact that in the case of tungsten (*a*) the absorption wave-length, a_3, is slightly shorter than that of the highest frequency emission line of the L series, namely, γ_1; (*b*) the absorption wave-length, a_2, is a large fraction of one per cent longer than that of the emission line, γ_2; and (*c*) the absorption wave-length, a_1, is a large fraction of one per cent longer than the emission line, β_2. The measurements on which these conclusions were based were made under the same experimental conditions for both the emission and the absorption lines. We have not measured the L series of emission

lines for chemical elements of higher atomic numbers than that of tungsten with our spectrometer. Hence we cannot make a direct comparison between emission and absorption wave lengths obtained under the same experimental conditions for these elements. If we take the wave lengths recorded by Siegbahn and Friman,[4] we find that (a) our value for the absorption wave-length, La_2, is shorter than that of the emission line, γ_4, for each element and that the difference between the two increases slightly with the atomic number; (b) our value for the absorption wave length,

TABLE 1

CRITICAL ABSORPTION WAVE LENGTHS. L SERIES OF X RAYS

Grating Space for Calcite, $2d = (6.056 \pm 0.004) \times 10^{-8}$ cm

CHEMICAL ELEMENT	ATOMIC NUMBER	ABSORBING SCREEN	MEASURED BY	WAVE LENGTHS $\lambda \times 10^{8}$ cm		
				La_2	La_1	$L\beta_2$
Tungsten	74		de Broglie	1.215	1.085	
Tungsten	74	Na_2WO_4	Author's	1.2136 ± 1	1.0826 ± 5	1.021 ± 3
Platinum	78		Wagner	1.072	0.951	
Platinum	78		de Broglie	1.060	0.930	
Platinum	78	Metal	Author's	1.0703 ± 1	0.9521 ± 1	0.8885 ± 4
Gold	79		Wagner	1.042	0.914	
Gold	79		de Broglie	1.038	0.898	0.858
Gold	79	Metal	Author's	1.0384 ± 1	0.8981 ± 1	0.8601 ± 8
Mercury	80		de Broglie	1.006		
Mercury	80	$HgSO_4$	Author's	1.0067 ± 5	0.8766 ± 1	0.8415 ± 1
Thalium	81		de Broglie	0.974	0.840	
Thalium	81	$Tl_2(SO_4)_3$	Author's	0.9776 ± 1	0.8415 ± 1	0.8055 ± 14
Lead	82		de Broglie	0.945	0.811	
Lead	82	$Pb(NO_3)_2$	Author's	0.9497 ± 1	0.8133 ± 1	0.7861 ± 9
Bismuth	83		de Broglie	0.921	0.786	0.761
Bismuth	83	Metal $Bi(NO_3)_3$	Author's	0.9216 ± 1	0.7872 ± 1	0.7612 ± 8
Radium	88		de Broglie	0.802	0.670	
Thorium	90		de Broglie	0.757	0.624	0.604
Thorium	90	$Th(SO_4)_2$	Author's	0.7586 ± 1	0.6280 ± 1	0.6044 ± 7
Uranium	92		de Broglie	0.718	0.588	0.568
Uranium	92	Acetate	Author's	0.7211 ± 1	0.5979 ± 1	0.5765 ± 7

La_2, is longer than that of the emission line, γ_1, for tungsten and gold, but shorter for the other elements; (c) our value for the absorption wave-length, La_1, is longer than that of the emission line, β_2, for tungsten, gold, and thallium, but shorter for platinum and bismuth. The relative positions of these emission and absorption lines appear to be matters of considerable theoretical importance,[5] and this subject will be discussed at greater length in a future note.

The Wave-lengths as Functions of the Atomic Numbers: Many of the laws connecting X-ray wave-lenghts with each other, or with the atomic numbers of the chemical elements may be expressed most simply in terms

of the wave numbers, $1/\lambda$, or of the ratios of the frequencies of vibration to the Rydberg fundamental frequency for heavy atoms. In his classical memoirs on the wave lengths of characteristic X-rays Moseley called attention to the fact that the square root of the wave-number (or frequency) of a line in the X-ray spectrum of an element is very nearly a linear function of its atomic number. To test this relation in the case of critical

TABLE 2

CRITICAL ABSORPTION WAVE-NUMBERS. L SERIES OF X-RAYS

Values of $1/\lambda$ and of $\sqrt{1/\lambda}$

CHEMICAL ELEMENT	ATOMIC NUMBER	$1/\lambda$	$\sqrt{1/\lambda}$ L_{III}	DIFFERENCES
Tungsten	74	0.8240 ± 1	0.9077	
Platinum	78	0.9341 ± 3	0.9665	0.0147 ± 1
Gold	79	0.9631 ± 3	0.9814	0.0149 ± 3
Mercury	80	0.9933 ± 4	0.9966	0.0152 ± 4
Thalium	81	1.0229 ± 3	1.0114	0.0148 ± 4
Lead	82	1.0530 ± 3	1.0262	0.0148 ± 3
Bismuth	83	1.0851 ± 3	1.0417	0.0155 ± 3
Thorium	90	1.3164 ± 5	1.1473	0.0151 ± 1
Uranium	92	1.3862 ± 5	1.1774	0.0151 ± 2
			L_{II}	
Tungsten	74	0.9323 ± 5	0.9656	
Platinum	78	1.0728 ± 4	1.0358	0.0176 ± 1
Gold	79	1.1120 ± 4	1.0545	0.0187 ± 4
Mercury	80	1.1494 ± 4	1.0721	0.0176 ± 4
Thalium	81	1.1883 ± 5	1.0901	0.0180 ± 5
Lead	82	1.2295 ± 5	1.1088	0.0187 ± 5
Bismuth	83	1.2703 ± 4	1.1271	0.0182 ± 5
Thorium	90	1.5908 ± 8	1.2613	0.0192 ± 1
Uranium	92	1.6808 ± 8	1.2999	0.0193 ± 3
			L_{III}	
Tungsten	74	0.977 ± 3	0.988	
Platinum	78	1.1255 ± 12	1.0609	0.0182 ± 5
Gold	79	1.162 ± 1	1.0780	0.0171 ± 11
Mercury	80	1.200 ± 1	1.0953	0.0174 ± 11
Thalium	81	1.242 ± 2	1.1142	0.0189 ± 15
Lead	82	1.282 ± 2	1.1320	0.0178 ± 16
Bismuth	83	1.328 ± 2	1.1523	0.0203 ± 13
Thorium	90	1.655 ± 2	1.2863	0.0192 ± 2
Uranium	92	1.750 ± 2	1.3263	0.0200 ± 7

absorption data we have calculated the wave-numbers and the square roots of the wave numbers for all of our values. Column 3, in Table 2, contains the wave numbers and Column 4 their square roots. In Column 5 we have tabulated the increase in the value of $\sqrt{1/\lambda}$ per unit increase in the atomic number. It appears that these differences do not vary from

the average values of the differences in their neighborhoods by more than the estimated errors, except in one or two cases. In other words, the $\sqrt{1/\lambda}$ may be represented as a function of the atomic number by a smooth curve, from which the individual values do not differ by more than the experimental errors. In the case of the absorption band, L_{III}, this curve differs a small amount from a straight line. In the cases of the bands $L\alpha_2$ and $L\alpha_1$, however, the departures from the straight line law appear to be much greater. A very much more pronounced variation from the linear law has been noted in the case of the critical absorption frequencies associated with the K series of X rays.[2] These departures from the straight line law have been ascribed to the relativity change of mass with velocity of the electrons connected with the production of the X rays.

The fact that the values of $\sqrt{1/\lambda}$ do not differ from a smooth curve law by more than the indicated errors of measurement shows that our estimates of accuracy are substantially correct.

The Relation between the Emission and Absorption Frequencies.—It has been found by experiment that the difference between the critical absorption wave number of the K series and one of the critical absorption wave numbers of the L series equals the wave number of one of the α lines in the K series to within the limits of error. The experiments were performed with the X ray spectrum of tungsten. As the emission wave lengths in the K series have not been measured for chemical elements of higher atomic numbers than that of tungsten, we cannot test this law between the K and L series for the heavier elements. We can test the law, however, in the case of the L and M series of thorium and uranium, for here all the necessary data is available. The tables of Seeglahn and Friman[3] contain the emission wave lengths in the L series, and Stenström[4] has measured three absorption wave lengths in the M series for each of these two elements. Using our values of the L absorption wave lengths we have compiled the following table of wave numbers (Table 3).

TABLE 3

RELATION BETWEEN ABSORPTION AND EMISSION WAVE NUMBERS
L and M Series

		U		Th			U			Th	
Absorption	$L\alpha_1$ M_3	1 000	1 047	$L\alpha_1$	M_3	1 000	1 053	$L\alpha_1$	M_2	1 058	1 066
Emission		$L\alpha_1$	1 048		$L\alpha_1$	1 000	1 052				
Absorption	$L\alpha_1$ M_2	1 103	1 322	$L\alpha_1$	M_2	1 309	1 309	$L\alpha_1$	M_1	1 142	1 263
Emission		$L\beta_1$	1 108	1 319		$L\beta_1$	1 309	1 305			
Absorption	$L\alpha_1$ M_1	1 472	1 385	$L\alpha_1$	M_1	1 456	1 [illegible]	$L\alpha_1$	M_3	1 411	1 326
Emission									$L\beta_1$	1 408	1 319

It appears from this table that the wave numbers of the emission lines $L\alpha_1$ $L\alpha_2$ and $L\beta_1$ agree very well with the differences between the absorption wave numbers L_{III} M_3, L_{III} M_2, L_{III} M_1.

Judging from this data alone, there is some question as to whether the emission line $l\alpha_1$ belongs to the absorption difference La_2–Ma_1 or to La_1–Ma_2.

No emission lines have been observed in the spectrum of either thorium or uranium that correspond to the other absorption differences contained in the table.

Four emission lines have been found by Siegbahn and Friman in the spectra of both thorium and uranium in addition to those contained in our Table 3, namely, $l_1\beta_5\gamma_6$ and $\gamma_{2,3}$. The way in which the frequencies of the lines for different chemical elements vary with their atomic numbers[8] and the researches of Webster and Clark[9,5] on the voltages required to produce the lines in the spectrum of platinum indicate that l and β_2 belong to the same X ray group as α_1 and α_2, and therefore also to the absorption La_2. Similarly, γ_1 belongs to the absorption La_3. If these lines obey the frequency difference law, there must be critical absorption wave lengths at $\lambda = 2.37 \times 10^{-8}$ cm. and at $\lambda = 2.23 \times 10^{-8}$ cm. for thorium and uranium, respectively, to correspond with the emission line l. These wave lengths lie within the range of possible measurements, but the spectrum in their neighborhood has not been examined for critical absorption. Similarly, there should be critical absorption wave lengths at $\lambda = 16.2 \times 10^{-8}$ cm. for thorium and at $\lambda = 15.8 \times 10^{-8}$ cm. for uranium to correspond with the emission lines β_2 and γ_1. These wave lengths, however, lie beyond the range of wave-lengths that can be measured at present by means of crystal spectrometers.

It is well known that Bohr's theory of radiation explains very simply the above relation between emission and absorption wave-numbers. The relation, however, should not be absolutely exact, if, as Sommerfeld supposes, some of the atoms contain M orbits that are elliptic, and other atoms of the same chemical element contain M orbits that are circular. In this case the L absorption drops should have a complex structure. We have not been able to observe such a structure in the drops on our curves, and the effect must be exceedingly small, if it exits at all.

Theories have been developed by Rubinowicz[10] and Bohr,[11] according to which transfers of electrons between certain pairs of orbits cannot take place.[12] If we apply these theories to the data contained in Table 3, we find that according to both theories the transfers represented by Ma_1–La_1 and Ma_2–La_2 should occur. As a matter of fact, the corresponding lines, α_1 and β_1, are the strongest lines in the L series. According to Rubinowicz's theory the transfer Ma_2–La_1 should occur, but according to Bohr's theory it should not, unless the atom is in a field of force. The corresponding line, α_2, has been observed, but is relatively very faint. According to both theories the transfer Ma_1–La_2 should not occur, and, as noted above, the experiments do not indicate conclusively whether the line β_2 belongs to this combination or not. Both theories allow the transfer

Ma_3–La_1, but no line corresponding to it has been observed. The transfer Ma_3–La_2 can occur according to Rubinowicz's theory, but not according to Bohr's, and there is no line to correspond with it. The other transfers, involving La_2, are not covered by the theory, for it does not in its present form include a third L orbit.

Sommerfeld's L-Doublet Theory. Sommerfeld has worked out an interesting theory of the splitting up of the L series into two distinct parts, the L_α series doublet. An account of his reasoning may be found in his book, Atombau und Spektrallinien, Chapter 5. According to this theory the difference in frequency $\Delta\nu$ between the two parts of the L series is due to the difference between the energies of electrons travelling in circular orbits and of electrons travelling in elliptic orbits. Some atoms are supposed to have circular L orbits, and other atoms of the same chemical element, elliptic L orbits. The general equation (78), in the chapter referred to, for the difference, $\Delta\nu$, in wave number, reduces to

$$\frac{\Delta\nu}{\nu_\infty} = \frac{1}{\alpha^2}(N-\sigma_1)^4 \left[\frac{1}{(n-\sigma_2)^2} - \frac{1}{(n-\sigma_3)^2}\right] \qquad (1)$$

for the L_α doublet, where $\nu_\infty = 109737$ is Rydberg's fundamental wave number, $\alpha = \frac{2\pi e^2}{hc} = .007286$, $h = n(N-\sigma_1)$, N is the atomic number, and n, a correction term due to the influence of neighboring electrons in the atom. Sommerfeld has tested his theory by means of the wave-number differences between certain emission lines in the spectra of a great many chemical elements, and has deduced from the data the value $n = 3.63$. Although there is some difficulty in interpreting this value of the constant, n, we have used it to test the formula by means of our values of the critical absorption wave numbers.[1] According to the theory the wave-number difference in the doublet should equal the difference between the wave-numbers of the absorption bands La_1 and La_2.

TABLE 4

THE L-DOUBLET WAVE NUMBER DIFFERENCE ($\nu = 109.7$)

CHEMICAL ELEMENT	ATOMIC NUMBER	OBSERVED	CALCULATED		
			$n = 3.63$	$n = 3.81$	WAVELENGTH
Tungsten	74	0.1083 ± 6	0.1071	0.1081	0.1037
Platinum	78	0.1387 ± 7	0.1369	0.1384	0.1327
Gold	79	0.1489 ± 7	0.1453	0.1468	0.1411
Mercury	80	0.1561 ± 8	0.1540	0.1556	0.1496
Thalium	81	0.1654 ± 8	0.1631	0.1647	0.1587
Lead	80	0.1765 ± 8	0.1733	0.1751	0.1682
Bismuth	83	0.1852 ± 7	0.1836	0.1856	0.1782
Thorium	90	0.2744 ± 13	0.2713	0.2739	0.2630
Uranium	92	0.3036 ± 13	0.3021	0.3051	0.2941

Table 4 contains the observed wave number differences of the L doublet, with estimated errors of experiment, and also three sets of computed differences. The values given in Columns 4 and 5 have been calculated directly by the above formula (1) without expanding it into a series of ascending powers of h. It would be necessary to use six or more terms of such a series in order to attain the indicated accuracy.

The differences between the observed values and those computed, using Sommerfeld's value of $n = 3.63$, all have the same sign, and are distinctly greater than the errors of measurement. The values obtained with $n = 3.45$ compare more favorably with the experimental results, and indicate that with $n = 3.43$ the formula would give the observed differences, $\Delta\nu$, within the limits of error for nearly all the elements contained in the table. Even in this case there appears to be a small systematic variation between the theoretical and experimental frequency differences, as though the formula were nearly but not quite correct.

The constant n represents the repulsive force on an electron in the L orbit due to the electrons in the K orbit plus the force due to the other electrons in the L orbit. If n_1 and n_2 are the numbers of electrons in the K and the L orbits, respectively, $n = n_1 + s_{n_2}$ for circular orbits, where

$$s_n = \frac{1}{4}\sum_{s=1}^{s=n-1} \operatorname{cosec} \frac{s\pi}{n},$$

The values of n for elliptic orbits is assumed equal to that for circular orbits. There are, however, no values of n_1 and n_2 that agree exactly with the empirical values $n = 3.63, 3.45$ or 3.43. For $n_1 = 2$ and $n_2 = 5$ we have $n = 3.38$. Other evidence of the distribution of electrons in atoms indicates that this arrangement is highly improbable.

As a matter of fact, the theory in its present form does not take account entirely of the influence of all the electrons in the L orbit itself. When one electron is removed from this orbit, the other electrons change their positions relative to each other and to the nucleus. In calculating the change in the atom's energy envolved we must take account of the change in their energy also. A modification of Sommerfeld's formula which includes these energy changes may be obtained by taking the product of n_2 into the value of the right-hand member of equation (1), with $n = n_1 + s_{n_2}$, and subtracting from it the product of $n_2 - 1$ into the value of the same expression, with $n = n_1 + s_{n_2 - 1}$. Before computing wave-number differences from this modified formula we must assign definite values to n_1 and n_2. This gives a sort of theoretical value for n.

Column 6, in Table 4, contains wave-number differences calculated in this way with $n_1 = 2$ and $n_2 = 4$. They differ uniformly from the experimental results by about 3%.

The above suggested alterations in the theory, however, do not obviate

certain difficulties (discussed by Sommerfeld in his book) that we encounter, if we suppose that the orbits all lie in the same plane. Possibly these difficulties will disappear, when we study more thoroughly atomic models in which the orbits do not lie in the same plane.

[1] E. Wagner, *Ann. Physik, Leipzig*, March, 1915 (868).

[2] M. de Broglie, *J. Physique, Paris*, May June, 1916 (161), and *Paris C. R. Acad. Sci.*, Nov. 24, 1919 (962).

[3] Blake and Duane, *Physic. Rev., Ithaca*, Dec., 1917 (624), and Duane and Patterson, *Ibid.*, 1920.

[4] Siegbahn and Friman, *Phil. Mag., London*, April, 1916 (423), and Nov., 1916 (497).

[5] D. L. Webster, *Proc. Nat. Acad. Sci., Washington, D. C.*, Jan., 1920 (26).

[6] Duane and Hu, *Physic. Rev.*, June, 1918 (488); and Dec., 1919 (516), and Duane and Shimizu, *Ibid.*, Feb., 1919 (159) and Dec., 1919 (522).

[7] Duane and Shimizu, *Ibid.*, July, 1919 (67); Duane and Patterson, *Ibid.*, 1920, Duane and Stenström, *Ibid.*, April, 1920 (302); and *Proc. Nat. Acad. Sci.*, Aug. 1902.

[8] Stenström, *Doctor's Dissertation*, Lund, 1919.

[9] Webster and Clark, *Proc. Nat. Acad.*, March, 1917 (181).

[10] Rubinowicz, *Physik. Zs., Leipzig*, **19**, 1918 (441–465).

[11] Bohr, *Copenhagen Academy*, 1918.

[12] Compare Sommerfeld, *Atombau und Spektrallinien*, Chapter 6.

[13] Compare de Broglie *Paris, C. R. Acad. Sci.*, Nov. 24, 1919 (962).

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ON THE RELATIVE POSITIONS AND INTENSITIES OF LINES IN X-RAY SPECTRA

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Grouping of L Series Lines.—The wave-lengths of the lines in the L series of X-rays have been measured for a great many of the chemical elements by Siegbahn and Friman.[1] They have published graphs which represent the square roots of the frequencies of corresponding lines in the spectra of different elements as functions of the atomic number. The graphs for the lines 1, α_2, α_1, β_2 and β_5 are very nearly straight, indicating that the square roots of the corresponding frequencies are almost linear functions of the atomic numbers, whereas the graphs for the other lines are curved, indicating a marked departure from the linear law. This would seem to mean that we can divide the lines in the L series into at least two groups.

In his work on characteristic absorption de Broglie[2] found three critical absorption wave-lengths associated with the L series of gold, bismuth, thorium and uranium. The authors[3] have extended this, and have measured the third critical absorption wave-length as well as the other two for the elements they examined from tungsten to uranium both inclusive. The fact that three critical absorption wave-lengths appear in the L series of

each chemical element would seem to indicate the existence of at least three distinct groups of lines.

The researches of D. L. Webster and Harry Clark[4] on the voltages required to produce the various lines in the *L* series of platinum and on the way in which their intensities increase with increasing voltage confirm this, and prove further that the lines η, β_1, γ_1 and probably γ_2 belong to the second group.

The modern theory of line spectra, also, seems to indicate the splitting up of the *L* series into groups. The differences in frequency between certain lines in the first group and corresponding lines in the second group are very nearly equal to each other. These pairs of lines with nearly the same frequency interval are η 1, β_1 α_2, γ_1 β_2 and γ_2 β_5. Sommerfeld[5] explains this division of the *L* series into groups with a constant frequency difference on the assumption that one group of lines is due to electrons falling into an *L* orbit that is circular, and that the other group is produced by electrons falling into an *L* orbit that is elliptic. The equation he derives from his theory for the magnitude of the frequency difference fits the facts with considerable precision.

The following facts indicate that the critical absorption La_1 belongs to the first group of lines, and that the critical absorption La_2 belongs to the second group of lines. Firstly, the wave-length of the critical absorption La_1 lies not far from that of the line of shortest wave-length in the first group, and the wave-length of La_2 lies close to that of the line of shortest wave-length in the second group. Secondly, as the authors have shown,[3] the square root of the frequency of La_1 for the different elements is almost a linear function of the atomic number, while that of La_2 departs from the linear law in the same way as do those of the second group of lines in Siegbahn and Friman's graphs. Thirdly, the frequency difference between La_2 and La_1 equals to a high degree of precision that between the pairs of lines η–1, β_1–α_2 and γ_2–β_5 which were all measured by the authors[6] under the same experimental conditions for the tungsten spectrum. Fourthly, the frequency differences between La_2 and La_1 for the various chemical elements from tungsten to uranium[3] agree very well with Sommerfeld's formula. Fifthly, the values of the critical voltages of two of the groups of lines in the *L* series of platinum measured by Webster and Clark[4] (namely, 13.20 kilovolts and 11.45 kilovolts) agree very well with the values of the same quantities calculated by the quantum equation from our critical absorption wave-lengths (namely 13.26 kilovolts and 11.54 kilovolts).

Relative Position of Lines.—It has been shown by Duane and Hu[7] that the critical absorption wave-length associated with the *K* series of Rhodium is about one-third of a per cent shorter than that of the shortest line (the γ line) in that *K* series. Further, Duane and Stenström[8] have found that the difference between the wave-length of the critical absorption in

the K series of tungsten and that of its γ line amounts to about one-half of one per cent, the γ line having the longer wave-length. In the case of each element the wave lengths were measured under exactly the same experimental conditions, so that there can be no doubt but that the critical absorption wave length in the K series is shorter than the wave-length of the γ line by an amount that considerably exceeds the errors of experiment.

Turning to the L series we find that the third critical absorption wave-length, La_3, appears to be shorter than that of the line of shortest wave-length in the L series, namely, γ_4.[3] The authors[6] have found the following values for these wave-lengths, $La_3 = 1.024 \pm 3$ and $\gamma_4 = 1.0261 \pm 6$, in the spectrum of tungsten. In the other two groups, however, the critical absorption wave-lengths are longer than those of the shortest wave-length lines respectively. In the tungsten spectrum the authors[3,6] found for the wave lengths in the first group $La_1 = 1.2136 \pm 1$ and $\beta_5 = 1.2040 \pm 7$, and in the second $La_2 = 1.0726 \pm 5$ and $\gamma_2 = 1.0655 \pm 4$. In each case the difference between the two wave-lengths considerably exceeds the estimated errors of experiment.

As the relative position of these emission and absorption lines appears to be a matter of considerable theoretical importance the authors have repeated their experiments in a slightly different form. To make doubly sure of the facts they have taken the readings so as to show the position of the critical absorption and those of the emission lines on each side of it on one and the same curve. The experimental conditions were exactly the same as those in the experiments described in the article referred to,[6] except that the X ray tube was turned so that the rays left the target making a slightly smaller angle with its surface than in the earlier experiments. This increased the absorption of the rays by the target itself, and made the absorption drop in the curves more prominent.

The curve in figure 1 represents the intensity of the radiation (measured by the currents in the X-ray spectrometer's ionization chamber) as a function of the crystal table angles. The drop in the curve marked a_1 corresponds to the critical absorption belonging to the first group of L series emission lines. The absorption of its own rays by the tungsten target alone produced this drop, as no absorbing screen was introduced in the path of the rays in this experiment. The tall peak on the curve represents the relatively strong emission line β_2. Its separation from the absorption drop corresponds very well with the wave-length interval between the two, calculated from the data obtained in the earlier experiments, namely 0.0283 ± 2. The small hump in the curve on the other side of the absorption drop represents the emission line, β_5.

This experiment proves conclusively that the critical absorption lies between the emission lines β_2 and β_5, in other words it has a longer wave-length than that of β_5.

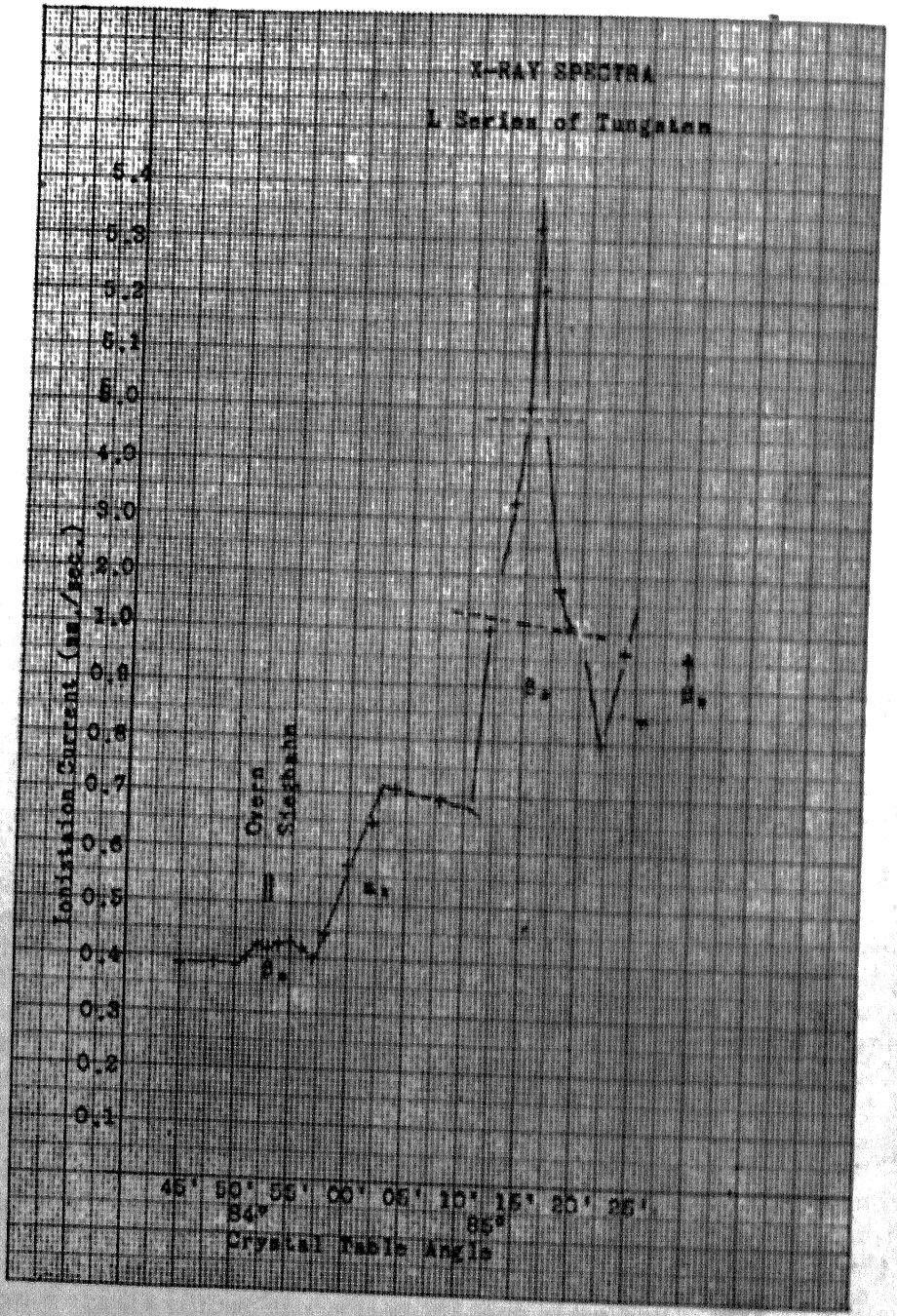

X-RAY SPECTRA
L Series of Tungsten
Ionization Current (mm./sec.)
5.4
5.3
5.2
5.1
5.0
4.0
3.0
2.0
1.0
0.8
0.6
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Ryerson
Stephahn
β_2
α_1
β_1
γ_1
45' 50' 55' 00' 05' 10' 15' 20' 25'
84°
85°
Crystal Table Angle

FIG. 1

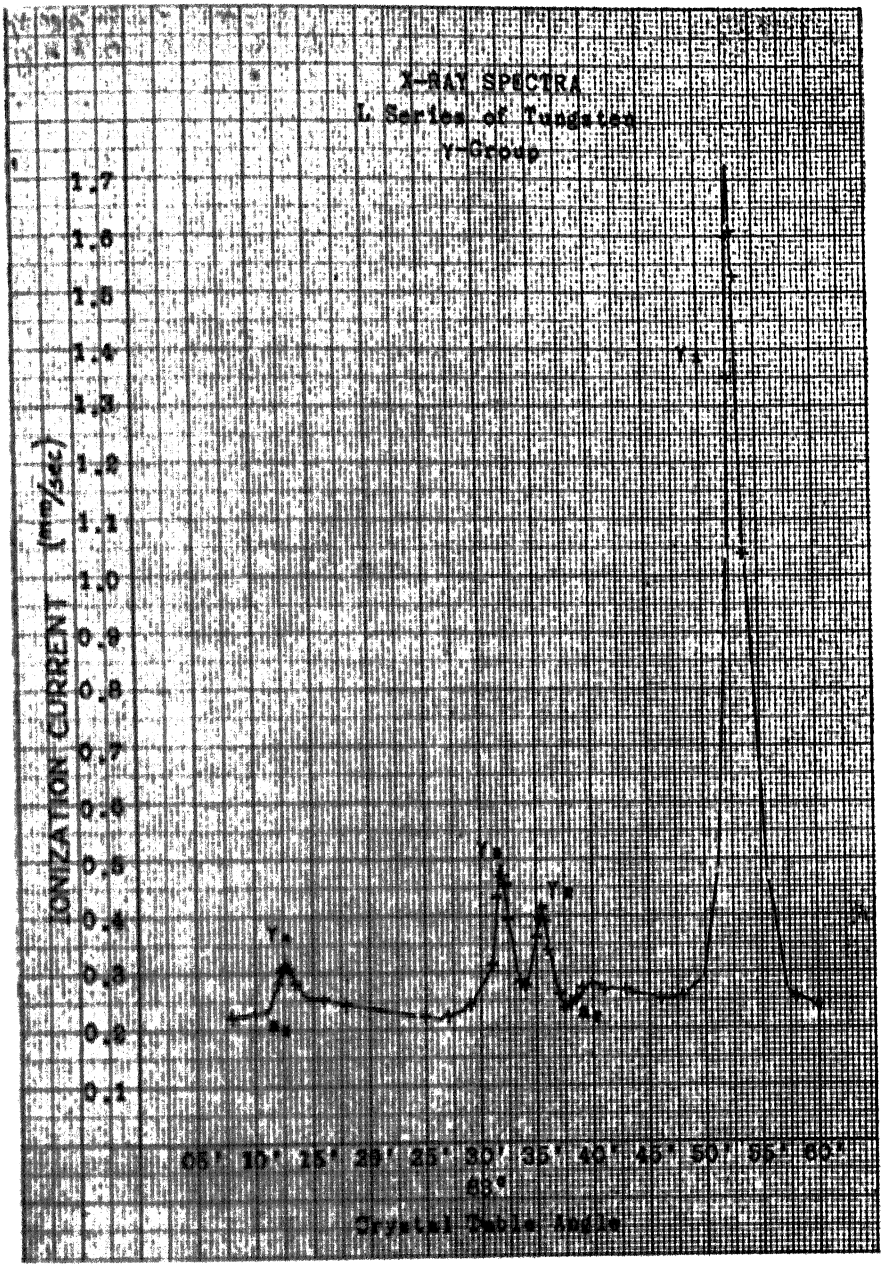

X-RAY SPECTRA
L Series of Tungsten
Y-Group
IONIZATION CURRENT (mm/sec)
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Y1
Y2
Y3
Y4
Y5
Y6
05° 10° 15° 20° 25° 30° 35° 40° 45° 50° 55° 60° 65°
Crystal Table Angle

FIG. 2

The positions of β_5 as determined from the measurements of Overn[9] and Siegbahn[10] are marked above the curve in figure 1. According to their measurements this faint line has a wave length a small fraction of one per cent shorter than our value, which would bring it still further from the critical absorption in the direction of shorter wave lengths.

The curve in figure 2 represents the spectrum of tungsten in the neighborhood of the critical absorption La_2. The drop corresponding to the absorption and the peaks corresponding to the γ emission lines appear on the curve. The critical absorption lies between the emission lines γ_1 and γ_2, and therefore has a wave-length longer than that of γ_2. Overn's and Siegbahn's values for γ_2 are in exact agreement with our values.

According to the conception of radiation held by many scientists the critical absorption wave-length corresponds to the short wave length limit of the group or series of emission lines with which it is associated. If this be true, or, to speak more accurately, if the term "group of lines" is defined in such a way that this is true, then β_5 cannot belong to the first group in the L series of X-rays, and γ_2 cannot belong to the second group.

The strongest evidence in favor of believing that β_5 belongs to the same *atomic mechanism* that produces the lines in the first group appears to be that the square root of its frequency increases from atom to atom nearly as a linear function of the atomic number, corresponding in this respect to all the lines in the first group but not to those in the second and third groups. In terms of the theory of atomic orbits this means that electrons falling into the L_1 orbit produce the line β_5, as they do all the lines in group 1. Webster and Clark[4] found that β_5 in the platinum spectrum appeared at a lower voltage than that required to produce the lines in the second group. This proves conclusively that β_5 cannot belong to the second group. The experiments on critical potentials, however, are not sufficiently accurate to decide whether β_5 appears at *exactly* the same voltage as the other lines in group 1, for β_5 is a weak line, and the difference between its wave-length and that of the critical absorption L_1 amounts to only 0.7% for tungsten. We are not, therefore, compelled to assume that β_5 can be produced by electrons in the X-ray tube having quantities of energy less than that given by the quantum equation, $Ve = h\nu$.

The argument in favor of supposing that the line γ_2 belongs to the mechanism that produces the lines in the second group rests largely upon the fact that for the various chemical elements the difference in frequency between γ_2 and β_5 equals the frequency interval between the lines in the other pairs belonging respectively to the two groups. It also equals the difference in frequency between the two critical absorptions La_2 and La_1, and is given quite accurately by Sommerfeld's L doublet formula. Hence, according to the theory of electron orbits, γ_2, in common with the

other lines belonging to the second group, is produced by electrons falling into the second, L_2, orbit.

On the experimental and theoretical evidence we have reached the conclusion that the emission line β_5 belongs to the atomic mechanism that produces the lines in the L_1 group, and that γ_2 belongs to that producing the lines in the L_2 group. On the other hand our experiments prove conclusively that the wave length of β_5 is shorter than that of the La_1 critical absorption, and that the wave-length of γ_2 is shorter than that of La_2. A somewhat similar situation occurs in the spectra of ordinary light. Here we have resonance and ionization potentials. There is a difference, however, between the character of the absorption of X-rays and that of ordinary light.

The best way of explaining these phenomena may be somewhat as follows. Let us suppose that the critical absorption La_1 corresponds to the transfer of an electron from the L_1 orbit to the periphery of the atom—to an orbit there where it can find a place to stick. This does not mean a transfer to an indefinitely great distance from the centre of the atom. There may be many orbits outside that at the periphery, even in addition to those that belong to visible spectra. With the electron in the orbit at the periphery the atom is in a state such that by the transfer of an electron back to fill the vacancy in the L_1 orbit it can radiate any one of the emission lines 1, α_2, α_1, β_2, etc., but not β_5. If, now, the frequency of the incident X ray beam is higher than that of the critical absorption, if the energy $h\nu$ is greater than that required to lift the electron to the periphery of the atom, it may carry the electron to an orbit further out or even outside of the atom altogether. In this case the atom would be in a state such that the return of an electron from one of these outside orbits would emit X radiation of higher frequency and shorter wave-length than that of the critical absorption. This would correspond to the emission line β_5. A similar explanation applies also to the emission line γ_2, and the L_2 orbit.

From this point of view we would expect the critical potential for β_5 to be slightly higher than that for the other lines belonging to the L_1 orbit, and the critical potential for γ_2 to be slightly higher than that for the lines associated with the L_2 orbit.

Further, on this theory, the critical absorption does not correspond to the limit of the group, or series. It becomes incorrect to speak of the "absorption limit," as these words are usually employed.

An accurate, quantitative test for our point of view cannot be obtained without making special assumptions. According to our measurements, however, the difference in frequency between the emission line and the critical absorption for tungsten, each divided by the Rydberg constant, is 6.0 for β_5 La_1, and 5.6 for γ_2–La_2. These are of the order of magnitude of frequencies associated with the peripheries of atoms.

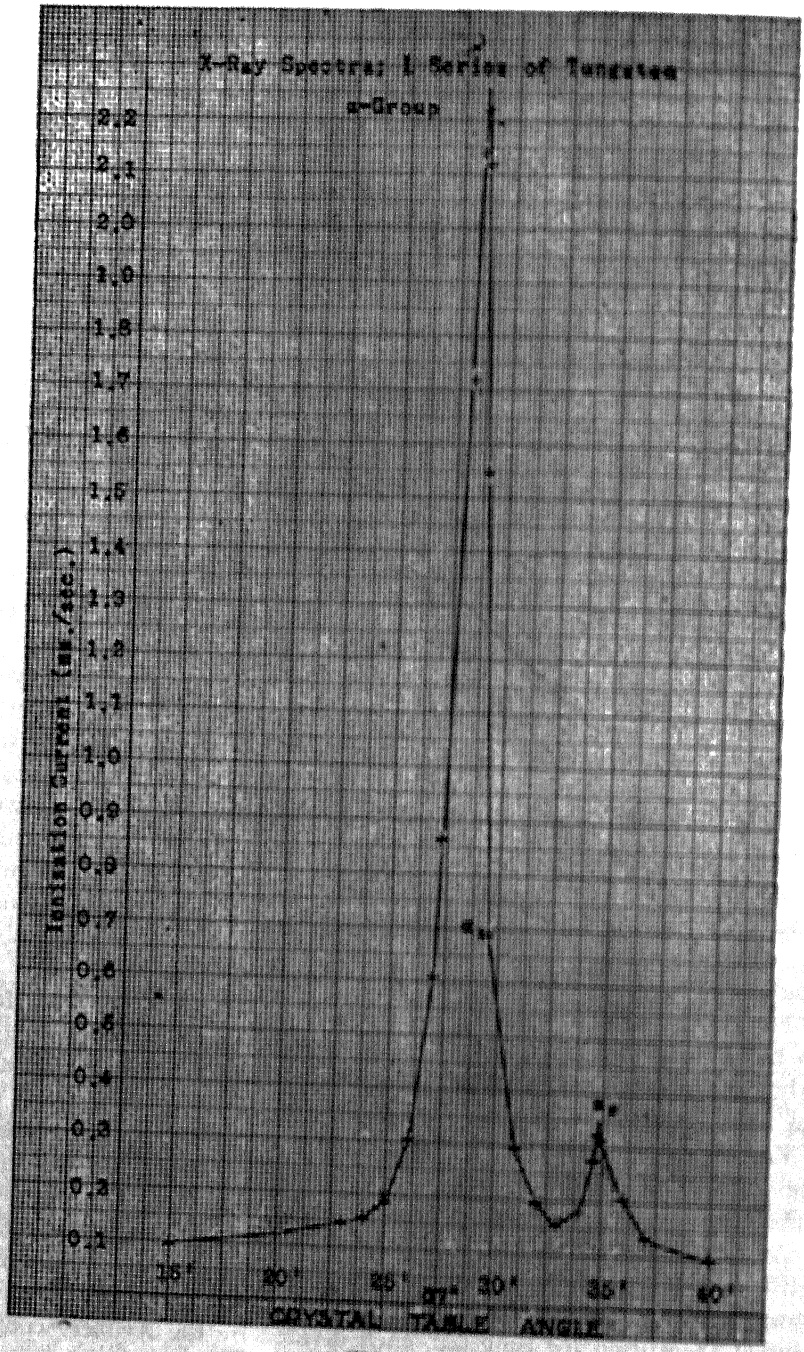

X-Ray Spectra: L Series of Tungsten
α-Group
Ionization Current (ue./sec.)
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
α_1
α_2
25°
30°
35°
40°
CRYSTAL TABLE ANGLE

FIG. 8

The question now arises as to whether or not an L critical ionization frequency equals an L critical absorption frequency. A critical ionization frequency represents the transfer of an electron completely *outside* of an atom. In the case of the K series of iodine the two frequencies have been found to be equal to each other within the limits of error of the measurements.[3] Experiments are in progress to test this point for the L series.

Relative Intensities of Lines. The ionization spectrometer provides us with an excellent method of estimating the relative intensities of lines in X ray spectra. Accurate estimates of the relative intensities, however, cannot be obtained unless the lines lie fairly close together. If a considerable interval separates them, corrections must be applied for the changes with varying wave length in the amounts of energy absorbed by the substances through which the rays pass, etc. These corrections cannot be accurately calculated at present. Special precautions must be taken to make sure that no critical absorption nor critical ionization wave length lies between the wave-length of the lines to be compared with each other. These limits to the accuracy of relative intensity measurements present themselves in photographic spectrometry in addition to those due to the difficulty of estimating the blackening of the photographic plates.

In the case of a line that is not perceptibly broadened we take the height of the peak corresponding to it on the ionization current crystal table angle graph to represent its intensity. This height must be measured from the level of the curve corresponding to the general radiation on the two sides of the peak, and not from the axis of zero ionization current.

Two peaks appear on the curve in figure 1, corresponding to the spectral lines β_2 and β_5. The ratio of the heights of these two peaks is 116. This number, however, does not represent accurately the relative intensity of β_2 to β_5, for the critical absorption of La_1 lies between the two emission lines. The target absorbs a greater fraction of the X-ray energy in the neighborhood of β_5 than it does in the neighborhood of β_2. In this case, therefore, the ratio of the heights of the peaks gives us only an upper limit for the ratio of the intensities. β_2 cannot be more than 116 times as intense as β_5.

The curve in figure 2 contains four peaks corresponding to the emission lines γ_1, γ_2, γ_3 and γ_4. The relative heights of these peaks are represented by the numbers 100, 14, 18 and 6. These numbers have not been corrected for the errors due to absorption, etc., so that they give only an approximate estimate of the relative intensities of the emission lines. The lines γ_2 and γ_3, however, lie very close together, and the correction must be very small. Since the critical voltages for all the γ lines are not quite the same, their relative intensities depend somewhat on the voltage

applied to the X-ray tube. This was 22,750 volts. The applied voltage lies so far above the critical voltages, however, that the effect due to variations in the latter do not amount to as much as three per cent.

Figure 2 in the paper referred to above[6] contains curves representing the four strongest β lines. The heights of the peaks corresponding to β_1, β_2, β_3 and β_4 are proportional respectively to the numbers 100, 55, 16 and 9; the voltage applied to the tube in this experiment being 24,800 volts.

The ratio of intensities of the two α emission lines possesses special theoretical interest. Sommerfeld[5] has developed a theory which predicts the relative intensity of certain lines in the spectrum. By applying the quantum theory to electron orbits that do not lie in the same plane he finds that the number of postitions which the plane of an orbit can occupy is greater by unity than the quantum number associated with the electron's angular coördinate. According to a line of reasoning due to Bohr[11] one of these positions is in a certain sense dynamically impossible, which reduces the number of possible positions the plane of the orbit can occupy by unity. According to Sommerfeld's theory all the possible positions of the orbit's plane are equally probably, and hence the intensity of the line is proportional to the number of possible positions.

In the case of the α lines in the K series this theory agrees very well with the facts.[8] The α lines in the L series, however, do not have the relative intensity predicted by the theory. The eletrons producing these α lines fall from M orbits into the same L_3 orbit. Those producing the α_1 line fall from the first, M_3, orbit, which has three quanta associated with the angular coördinates, while those producing the α_2 line come from the orbit M_2, which has only two quanta associated with the angular coördinates. According to Sommerfeld, therefore, the relative intensities should be in the ratio of 4 to 3. As a matter of fact, the ratio is very much larger than this. The curve in figure 3 represents the two α lines in the L series of tungsten. The ratio of the heights of the two peaks is about 10 to 1. According to Bohr's "analogue principle" the transfer from M_2 to L_3 could not take place, unless the atom were in a field of force. This may account for the weakness of the α_2 line.

[1] Siegbahn and Friman, *Phil. Mag., London*, April, 1916 (403); and Nov. 1916 (407).
[2] de Broglie, *J. Physique, Paris*, May–June, 1916 (161).
[3] Duane and Patterson, *Proc. Nat. Acad Sci., Washington*, Sept. 1920.
[4] Webster and Clark, *Ibid.*, March, 1916; and Webster, *Ibid.*, Jan., 1920.
[5] Sommerfeld, *Atombau und Spektrallinien*.
[6] Duane and Patterson, *Physic. Rev., Ithaca*, 1920.
[7] Duane and Hu, *Ibid.*, Oct., 1919 (369).
[8] Duane and Stenström, *Ibid.*, April, 1920 (329); and *Proc. Nat. Acad. Sci. Washington*, Aug., 1920.
[9] Overn, *Physic. Rev.*, Aug., 1919 (137).
[10] Siegbahn, *Phil. Mag.*, Nov., 1919 (639).
[11] Bohr, *Copenhagen Academy*, 1918.

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THE ABSORPTION OF X-RAYS BY CHEMICAL ELEMENTS OF HIGH ATOMIC NUMBERS

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Introduction. A critical absorption wave-length characteristic of a chemical element is a wave length such that the element absorbs X-rays longer than the critical value less than it does X-rays shorter than that value. Each chemical element has one critical absorption wave-length associated with its K series of characteristic emission lines. Duane and Hu[1] have shown that in the K series of rhodium the critical absorption wave-length is about one-fourth of one per cent shorter than that of the shortest line (the γ line) in the K emission series. The authors[2] found that the critical absorption in the K series of tungsten has a wave-length of about one-half of one per cent shorter than that of the $K\gamma$ emission line. Since the other characteristic X-ray series have longer wave-lengths than those of the K series, the K critical absorption wave-length is the shortest X-ray wave length now known to be characteristic of a chemical element.

In the research described in this note the authors have measured the critical absorption wave-lengths in the K series of most of the available chemical elements from tungsten to uranium, both inclusive. They used an ionization spectrometer, and examined spectra of the first, second and third orders. In 1918 Duane and Shimizu[3] measured four of these wave-lengths in spectra of the first order by the ionization method. Measurements with the same spectrometer of the K critical absorption had previously been made for most of the chemical elements down to man-

ganese (atomic number 25).[4] De Broglie[5] and Siegbahn and Jonsson[6] have published measurements of the K critical absorption by means of photographic spectrometers for the chemical elements of high atomic numbers included in this research. They examined spectra of the first order. Columns 3 and 4 in the table contain the values of the wave-lengths they give.

Apparatus and Method. The general method of making the measurements does not differ essentially from that employed by Duane and Shimizu.[3] We have been able, however, to apply a somewhat higher voltage to the X-ray tube than in the earlier researches. The X ray tubes we have used do not withstand a *constant* difference of potential greater than about 115,000 volts. To produce X rays shorter than the K series of uranium, however, requires a voltage considerably in excess of this figure. By encasing the arms of the X ray tube and also those of the kenotrons belonging to the high tension generating plant in oil baths we have been able to excite the tube with approximately constant voltages up to about 140,000 volts. We estimated these voltages with an electrostatic voltmeter, which we calibrated by measuring the current from the generating plant through a series of coils of manganin wire having a total resistance of 6,043,000 ohms. As a check on the voltage measurements and on the constancy of the difference of potential we determined the short wave-length limit of the general X ray spectrum and calculated the voltage by means of the quantum equation $Ve = h\nu$. Duane and Hunt[7] showed by experiments that this law holds for the limit of the spectrum, and their results have been verified by more recent researches.

Results of the Measurements. On platting the currents in the ionization chamber against the angular positions of the table on the spectrometer that supports the crystal we obtain curves, examples of which appear in figures 1 and 2. The sharp drops, a, in these curves, represent the critical absorption due to the chemical element under investigation. A layer of matter containing this element is placed in the path of the X-rays between the X-ray tube and the spectrometer. The angular distance between the mid points in corresponding drops on the two sides of the zero gives us twice the glancing angle, θ, which must be substituted in the usual formula,

$$\lambda = 2d \sin \theta$$

to calculate the critical absorption wave length. A correction for excentricity, amounting to about 27″ of arc, has to be subtracted from the values of θ measured on the graphs.

One pair of curves in figure 1 represents the critical absorption of uranium. These curves are of special interest, for they correspond to the shortest characteristic X-ray (of any chemical element) that has been discovered up to the present time. The centres of the drops can be

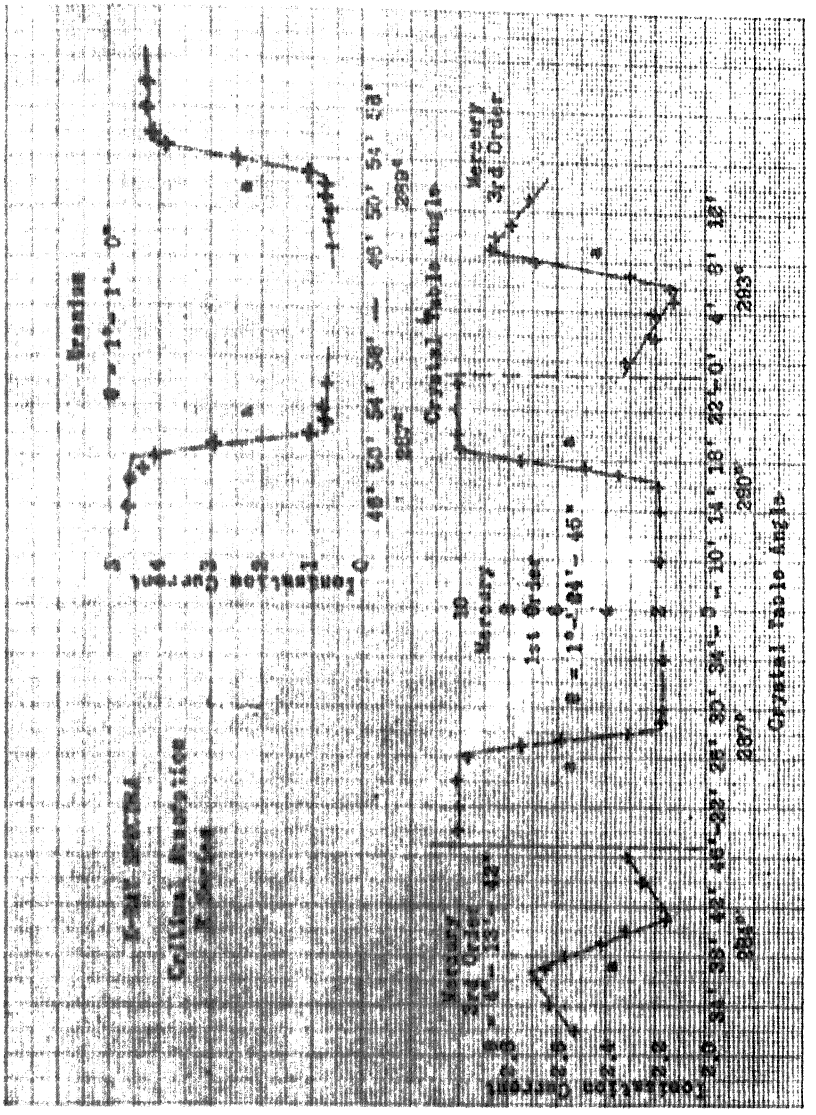


FIG. 1

estimated with reasonable certainty to within about 10″ of arc, and, as θ equals 61′ in this case, the error of precision amounts to less than one-third of one per cent

The other curves in figure 1 and the curves in figure 2 belong to mercury and bismuth, respectively. One pair of curves represents the critical absorption of bismuth in the second order spectrum, and another pair, the critical absorption of mercury in the third order. The drops corresponding to the absorption in the second and third order spectra are very much smaller than in the first order, and for this reason it is

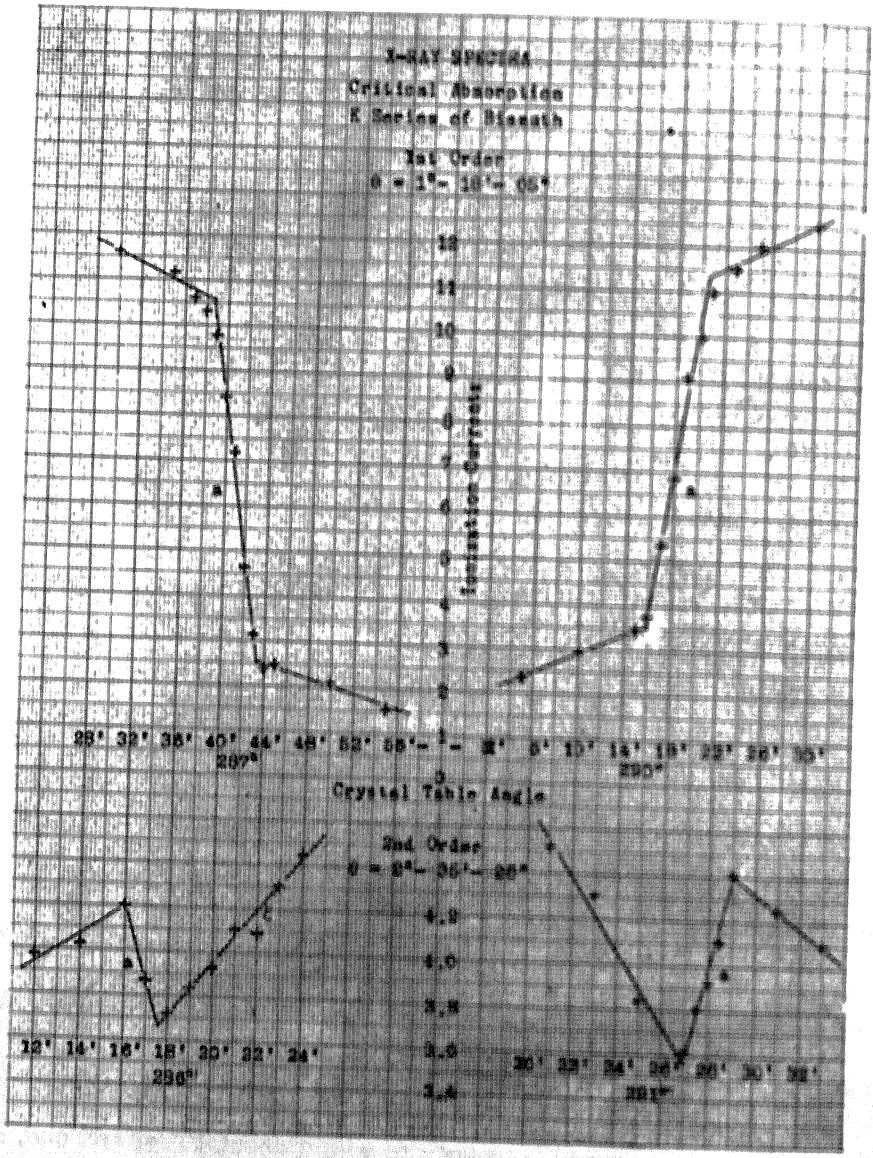


FIG. 2

more difficult to estimate their centers. The value of θ, however, is two or three times as large as in the first order.

Columns 5, 6 and 7 in table 1 contain the critical absorption wave-lengths estimated from the curves of figures 1 and 2 (and similar curves for the other chemical elements) in the spectra of the first, second and third orders respectively. Column 8 contains weighted mean values of the wave-lengths, column 9, the square roots of the wave-numbers, and

TABLE 1.

K CRITICAL ABSORPTION WAVE-LENGTHS, $\lambda \times 10^8$ Cm.

For Calcite $\lambda = 6.056 \times \sin\theta \times 10^{-8}$ Cm.

CHEMICAL ELEMENT	ATOMIC NUMBER	DE BROGLIE	SIEGBAHN	AUTHORS' VALUES					
				1ST	2ND	3RD	AVERAGE	$\sqrt{1/\lambda} \times 10^{-4}$	DIF.
Tungsten*	74			.1783	.1781	.1780	.1781	2.370	
Platinum	78	152	1578	.1582	.....	.1581	.1581	2.515	.036
Gold	79	149	1524	.1537	.....	.1532	.1534	2.553	.038
Mercury	80	146	1479	.1493	.....	.1488	.1491	2.590	.037
Thallium	81	142	1427	.1448	.....	.1449	.1448	2.628	.038
Lead	82	138	1385	.1412	.1409	.....	.1410	2.663	.035
Bismuth	83	133	1346	.1375	.1369	.....	.1372	2.700	.037
Thorium	90		1127	.1139	.1124	.....	.1131	2.974	.039
Uranium	92		1048	.1075	.....	.....	.1075	3.051	.037

* The wave-lengths for tungsten were measured in coöperation with Dr. R. A. Patterson

column 10, the difference, between these square roots calculated per unit increase in atomic number.

Discussion of the Results.—The differences tabulated in column 10 do not vary from their mean value more than one would expect from the experimental errors. This indicates that within the limits of error $\sqrt{1/\lambda}$ is a uniformly increasing function of the atomic number. The differences, however, are slightly larger than the corresponding differences between the square roots of the critical absorption wave-numbers measured in previous researches[3,4] for chemical elements of lower atomic numbers. This means that the square root of the critical absorption wave-number is not quite a linear function of the atomic number, which agrees with the results noted in the earlier papers.[3,4] The variation from the linear law, however, is too small to be clearly indicated in the range of values contained in table 1.

The wave-lengths measured in spectra of the second and third order (columns 6 and 7) appear to be, with one exception, smaller than the corresponding wave-lengths measured in the first order spectrum. The differences between the two sets of values about equal the errors of measurement. Similar differences between spectra of the various orders were observed first by Dr. Stenström[5] in his measurements of long X-rays by means of a photographic spectrometer. He attributed the effect to a slight refraction and dispersion of the X-rays by the reflecting crystal.

Our measurements in the second order spectrum for thorium were not

as satisfactory as the others. The generating plant had to be pushed to the limit of its capacity, and the fluctuations in the X ray output were unusually large.

Our values of the wave lengths are uniformly larger than those obtained by photographic methods. On the average these differences amount to between one and two per cent. The measurements by Siegbahn and Jönsson were made with an interesting spectrometer specially designed to eliminate errors due to the penetration of the X rays into the reflecting crystal, etc. In an ordinary spectrometer, if the grazing angle θ, is determined by the position of the reflected beam of X rays these errors may be either positive or negative, according to the position of the axis of rotation of the crystal with reference to what we have called the *effective* reflecting plane. Further, they may increase or decrease with the wave length of the rays, and in limiting cases the size of the crystal would have an effect on them. Our method of using the spectrometer eliminates these errors, for we determine the grazing angle, θ, from the angle through which the crystal turns and not by the position of the reflected beam. The differences, therefore, between our values and those given by Siegbahn and Jönsson cannot be ascribed to errors of this kind. Possibly they may be due to differences in the manner of interpreting the experimental observations. If, for instance, measurements on a photographic plate were made from the point where the plate *begins* to get dark, the corresponding value of the critical absorption wave length would be shorter than that given by our method, for we measure between points half way up the steep drops. The point where the photographic plate begins to darken corresponds to the bottom of a drop on our curves.

The wave lengths contained in table 1 complete the series of measurements of the K critical absorption of the chemical elements that we have been making in our X-ray laboratory during the past few years.[1] We now have values of the K critical absorption wave lengths for most of the chemical elements from manganese (atomic number 25) to uranium (atomic number 92) both inclusive. These wave lengths have been measured by means of the same ionization spectrometer and with the same calcite crystal, and are therefore comparable with each other.

[1] Duane and Hu, *Physic. Rev., Ithaca, N. Y.*, Oct., 1918 (360).
[2] Duane and Stenström, *Washington Nat. Acad. Proc.*, Aug., 1920.
[3] Duane and Shimizu, *Physic. Rev.*, Dec., 1919 (522).
[4] Blake and Duane, *Ibid.*, Dec., 1917, 697, and Duane and Hu, *Ibid.*, Dec., 1919 (518).
[5] De Broglie, *J. Physique, Paris*, May–June, 1916 (161).
[6] Siegbahn and Jönsson, *Physik. Zeits.*, 1919 (251).
[7] Duane and Hunt, *Physic. Rev.*, Aug., 1915 (166).
[8] Stenström, Doctor's *Dissertation*, Lund, 1919.

ON THE X RAY SPECTRA OF TUNGSTEN.[1]

By William Duane and R. A. Patterson.

Synopsis.

Critical Absorption and Emission Wave-lengths in K and L Series.—This paper describes accurate measurements of the critical absorption wave-lengths associated with the K and the L series, and also of the wave-lengths of most of the emission lines in the L series. The measurements were made by means of a new ionization spectrometer, similar to the one described in the PHYSICAL REVIEW for Dec., 1915, at page 644. A high tension storage battery supplied the current through the X ray tube, the voltage and current being kept constant by the procedure indicated in the reference. To eliminate errors due to the penetration of the rays into the crystal and to lack of exact adjustment between the axis of rotation of the crystal and the *effective* reflecting plane, etc., the authors employed the third method mentioned in the article referred to, above. In this method two slits between the X ray tube and the spectrometer define the width of the beam of X rays that strikes the crystal, and the slit in front of the ionization chamber has sufficient breadth to allow the entire reflected beam to enter the chamber. With this arrangement of slits the angle through which the crystal turns (not the angle made by the *reflected* beam of rays with the *zero* of the instrument) measures the glancing angle that is used in the formula to calculate the wave-length.

Mean Values of the Wave-lengths Measured in Spectra of the 1st, 2d and 3d Orders.—The following table contains the weighted mean values of the wave-lengths obtained from measurements in spectra of the 1st, 2d and 3d orders, together with an estimate of the precision of the measurements. To estimate the *absolute* accuracy of the data we must take into account the errors in the value of the grating constant of the calcite crystal used. These add up to about 0.07 per cent. In the text the values of the emission wave-lengths obtained by this ionization method are compared with those measurements of the same lines by photographic methods in which special procedures have been employed to minimize the effects of the above mentioned errors.

X Ray Spectra of Tungsten.

Grating Constant for Calcite $2d = (6.056 \pm .004) \times 10^{-8}$ cm.

Critical Absorption Wave-Lengths, $\lambda \times 10^8$ cm.

K	L_{α_1}	L_{α_2}	L_{α_3}
.17806 ± 7	1.2146 ± 1	1.0726 ± 5	1.024 ± 3

Emission Wave-Lengths, $\lambda \times 10^8$ cm.

$K\alpha_1$	$K\alpha_2$	$K\beta$	$K\gamma$	
.21141 ± 4	.20860 ± 4	.18420 ± 3	.17901 ± 6	
$L\iota$	$L\alpha_2$	$L\alpha_1$	$L\eta$	
1.6756 ± 10	1.4849 ± 4	1.47306 ± 11	1.4176 ± 7	
$L\beta_4$	$L\beta_6$	$L\beta_2$	$L\beta_5$	$L\beta_5$
1.2985 ± 4	1.27892 ± 9	1.2601 ± 3	1.24193 ± 12	1.2040 ± 7
$L\gamma_2$	$L\gamma_3$	$L\gamma_1$	$L\gamma_4$	
1.09608 ± 7	1.0688 ± 4	1.0596 ± 3	1.0261 ± 6	

[1] A paper presented to the American Physical Society at its New York meeting, Feb. 28, 1920.

The Relative Intensity of the Lines.—The ionization spectrometer furnishes the best method of estimating the relative intensity, the relative breadth, etc., of emission and absorption lines, provided that they are so near together that the effect of absorption by the tube, etc., may be neglected or corrected for. The numerous curves in the text give a good idea of the relative intensity, etc., of the lines.

The Differences between the K and L Absorption Frequencies Equal the Ka Emission Frequencies in Each Case to Within the Errors of Measurement.—The object of the research has been to obtain accurate values of both the absorption and the emission wave-lengths measured under the same experimental conditions. This becomes particularly important in testing theoretical laws and relations. According to the theory of the mechanism of radiation based on the Rutherford-Bohr atomic model the K critical absorption frequency should be complex, if, as Sommerfeld assumes, some atoms contain elliptic orbits and other atoms of the same chemical element contain circular orbits. Further the difference between the *average* K critical absorption frequency and one of the L critical absorption frequencies should not exactly equal the frequency of one of the Ka emission lines. As a matter of fact the authors have not observed a doubling of the K absorption frequency, and their new measurements verify the results obtained last year by Duane and Shimizu.[1] The difference between the K absorption frequency and one of the L absorption frequencies equals the frequency of one of the Ka emission lines in each case to within the errors of measurement. Hence, if the effect due to different kinds of tungsten atoms exists at all, it is too small to be detected, at least for chemical elements of high atomic numbers.

Test of Sommerfeld's Formula for the Frequency Interval of the L Doublet.—A Sommerfeld[2] has deduced from Bohr's theory an expression for the frequency interval of the L series doublet by making an interesting application of one of the equations in the quantum theory, which enables him to calculate the eccentricity of an elliptic orbit. The expression contains one undetermined constant, to which he gives the value 3.63. This value he obtains by using the published wave-lengths of the lines in the L series of a great many chemical elements. Although there is some difficulty in giving a physical interpretation to the theory, yet, when one substitutes the constant in the formula, one obtains the frequency difference of the L series doublet in the tungsten spectrum to within less than one per cent of the value we found by experiment.

Object.—The object of the research reported in this paper has been to measure both the critical absorption and the emission wave-lengths associated with the K and the L series of tungsten. Values of these absorption and emission wave-lengths measured under the same experimental conditions are not available at present, and, evidently, for the purpose of testing certain relations deduced from theories of the structure of atoms and the mechanism of radiation, such a series of comparable wave-lengths should be obtained.

Apparatus and Method.—In order that the values of the wave-lengths might be as free as possible from errors due to the penetration of the X-rays into the reflecting crystal, and to lack of exact adjustment

[1] PHYSICAL REVIEW, July, 1919, p. 67.

[2] Atombau und Spektrallinien, Chapter 5.

between the axis of rotation of the crystal, the incident beam of rays, the *effective* reflecting plane in the crystal, etc., we have employed a new ionization spectrometer, similar to the one described in detail in the PHYSICAL REVIEW for December, 1917, at page 624. The new instrument does not differ essentially from the old one, but has circular scales that appear to be somewhat more exact. We were able to detect no difference between the readings of the two verniers attached to the crystal table that would give us a perceptible correction for excentricity in the parts of the scale used.

We have adopted the third method of arranging the spectrometer slits mentioned in the article referred to above. A narrow beam of X-rays, defined either by two slits in lead blocks between the X-ray tube and the spectrometer or by one slit and the focal spot on the target, falls on the reflecting crystal. The third slit, that in front of the ionization chamber, has sufficient breadth to allow the entire reflected beam to enter the chamber. The chief advantage of this arrangement lies in the fact that no correction is necessary for the penetration of the rays into the crystal and for the lack of exact adjustments in certain parts of the instrument. By taking readings corresponding to the same spectrum line on both sides of the zero, twice the glancing angle of incidence can be calculated by simply subtracting the angle through which the crystal has been turned from 180°. The angle through which the ionization table has been turned does not enter into the calculation. In those methods of using a spectrometer in which the glancing angle has to be calculated from positions of the reflected beam of rays (photographic methods, for instance) corrections for the above mentioned sources of error must be applied, or else special devices must be employed to eliminate them.

In making a series of measurements the crystal and ionization chamber are rotated through successive angular increments, the chamber always being moved twice as far as the crystal. In each position of the crystal the ionization current is measured. The graphs representing ionization currents as functions of the crystal table angles (see the figures) indicate peaks, corresponding to characteristic emission lines, and sharp drops, corresponding to characteristic absorption lines. To get the double glancing angle of incidence, 2θ, for substitution in the wave-length formula,

$$\lambda = 2a \times 10^{-8} \sin\theta \text{ cm.},$$

we measure from the tips of the peaks or the centers of the drops, as the case may be.

To sum up, the above described arrangement of slits and general

lying exactly in the effective reflecting plane, (c) the center of the incident beam not passing exactly through the axis of rotation and (d) certain of the defects in crystal structure.

A further advantage of the ionization method lies in the fact that very good estimates of the relative intensity of spectral lines may be

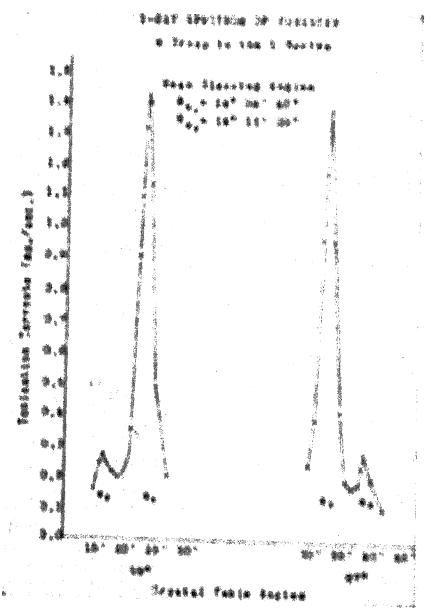


Fig. 1.

obtained, provided that the lines lie so close together that we may neglect, or correct for errors due to changes in the coefficients of absorption and of reflection with wave-length.

For the tungsten emission spectrum we used an X-ray tube of the Coolidge type equipped with a tungsten target. The rays emerged from the tube through a thin glass window blown in a side arm attached to it. This materially reduced the absorption of the relatively soft L series lines. The rays emerging through this window left the target at almost grazing angles. This gave so narrow a source of rays that only one slit was needed to make the incident pencil of rays as narrow as desired.

As in earlier researches a high tension storage battery supplied the current through the X-ray tube, the voltage being kept constant during an experiment by gradually changing a resistance in series with the tube.

The usual method of control of the current through the tube enabled

ture of the target, etc., constant.

We used a lead ionization chamber filled with methyliodide or ethylbromide and provided with a very thin mica window to reduce the absorption of the reflected beam of X-rays as it entered the chamber. A quadrant electrometer measured the ionization currents.

Tungsten L emission lines. Thirteen lines in the L series of tungsten have been measured. Figs. 1, 2 and 3 show typical curves platted from actual measurements on the α, β and γ groups of lines respectively. The position of a peak can always be located as between two crystal

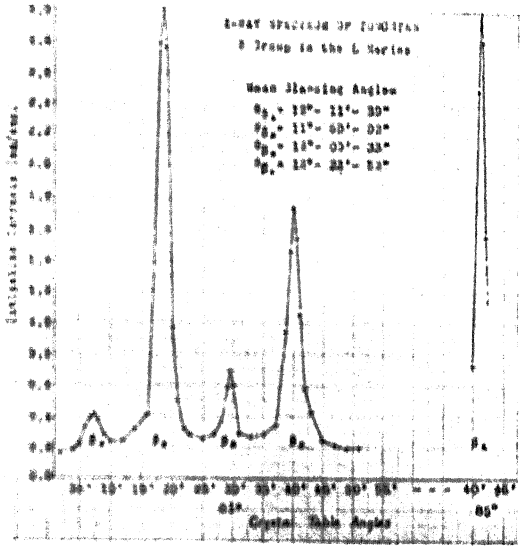


Fig. 2.

angle readings, 30″ of arc apart. Moreover, a good estimate may be made as to how much nearer the actual peak lies to one of these readings than to the other. We believe that, by making several complete series of measurements, we have been able to determine the value of the double glancing angle, 2θ, to within less than 10″ of arc in many cases. This means an error of not more than .01 to .02 of a per cent. in the value of the glancing angle, depending upon its magnitude. The grating space, d, of calcite is known to within about 0.07 of a per cent. No other grating space appears to have been determined as accurately as this. The best determinations of the grating space of calcite lie within a few hundredths of a per cent. of 3.028×10^{-8} cm. We have chosen this value, therefore, to use in calculating our wave-lengths. Hence, taking the grating space of calcite as fixed, we may assume that the relative

according to their magnitudes, in our best experiments.

The lines l, α_1, α_2, η, β_1, β_2, γ_1, and γ_2 have all been measured on both sides of the zero position of the crystal. The glancing angles for β_3, β_5

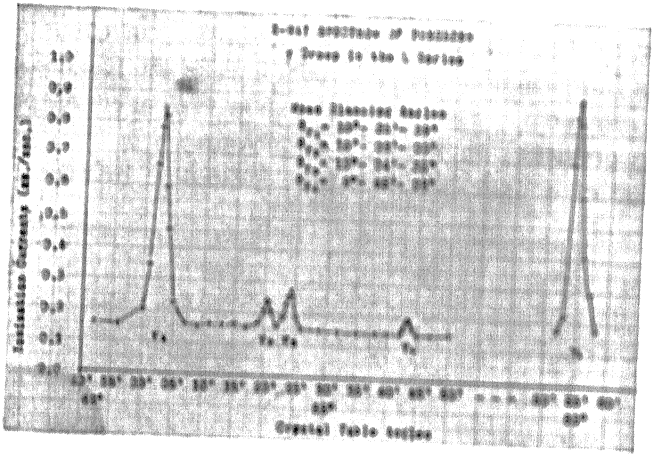


Fig. 3.

β_5, γ_2 and γ_4, however, have been determined by comparison with the glancing angles for neighboring strong lines.

Measurements of the glancing angles for α_1, β_1 and γ_1 have been

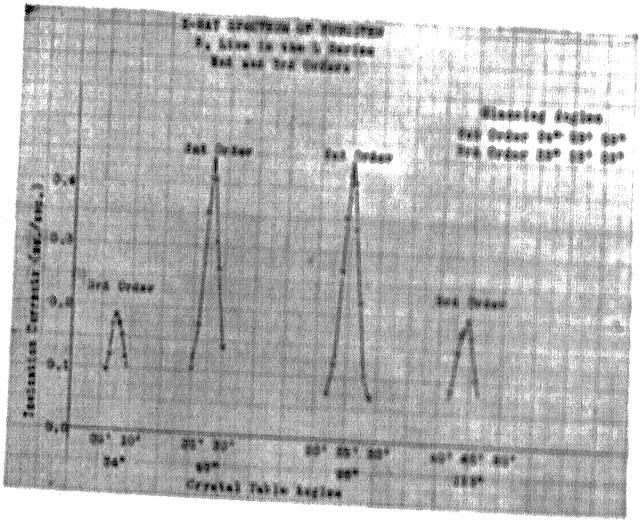


Fig. 4.

made in the first and second order spectra, and for β_1 also in the third order spectrum. Fig. 4 shows the curves obtained for β_1 in the second

and third order spectra. There is a slight indication in the third order spectrum that this line has a close and weaker satellite on its short wave-length side.

Table I. contains the glancing angles and computed wave-lengths for α_1, β_2 and γ_2.

TABLE I.

L Series of X-Rays.

Tungsten.

Grating Constant for Calcite $2d = 6.056 \times 10^{-8}$ cm.

Line.	Order.	Glancing Angle.	Wave-length $\times 10^8$ Cm.
α_2	1	14° 04′ 46″	1.47322
α_1	1	14° 04′ 39″	1.47303
α_1	3	29° 06′ 27″	1.47297
β_5	1	12° 11′ 32″	1.27898
β_3	1	12° 11′ 34″	1.27904
β_1	1	12° 11′ 35″	1.27907
β_2	1	12° 11′ 34″	1.27904
β_4	2	24° 58′ 59″	1.27886
β_5	4	39° 18′ 26″	1.27878
γ_4	1	10° 25′ 46″	1.09628
γ_3	1	10° 25′ 37″	1.09602
γ_4	2	21° 13′ 24″	1.09614
γ_2	2	21° 13′ 15″	1.09603

It is interesting to note that the wave-lengths computed from data in higher orders are slightly shorter than those computed from lower orders. Stenström[1] has found similar differences in the case of certain longer wave lengths which he measured by means of the crystals sugar and gypsum. He has ascribed the differences to a small amount of refraction and dispersion of the X-rays by the crystals. The differences here noted, however, are of the order of magnitude of the experimental errors.

The fourth column in Table II. contains our weighted mean values for the wave-lengths, measured in a number of complete series of experiments. For comparison we have tabulated the wave-lengths recorded by Overn[2] and by Siegbahn[3] in the second and sixth columns respectively. A slight correction, amounting to one thirtieth of one per cent., has been subtracted from the values they give in order to make their wave-lengths correspond to the grating constant for calcite that we use. Columns

[1] Doctor's Dissertation, Lund, 1919.

[2] Phys. Rev., Aug., 1919.

[3] Phil. Mag., Nov., 1919.

wave-lengths measured by the ionization method agree in most cases with those measured by the photographic method to within the limits of experimental errors. In each of the series of measurements by the photographic method great care was taken by the respective authors to

TABLE II.

L Series of X-Rays. $\lambda = 10^{-8}$ cm

Tungsten

Grating Constant for Calcite $2d = 6.046 \times 10^{-8}$ cm

Line.	Overn.	Difference.	Duane Patterson	Difference	Siegbahn
l			1.6256 ± 10	(.0005)	1.62448
α_2	1.4834	−.0005	1.48439 ± 4	(.0001)	1.48404
α_1	1.4726	−.0005	1.47306 ± 11	(.0001)	1.47269
η			1.4176 ± 7	(.0004)	1.4152
β_4	1.2980	−.0005	1.29855 ± 4	(.0001)	1.29831
β_1	1.2789	.0000	1.27892 ± 9	(.0002)	1.27874
β_3	1.2594	−.0007	1.2601 ± 4	(.0001)	1.25958
β_2	1.2430	+.0011	1.24194 ± 12	(.0003)	1.24150
β_5	1.2017	−.0024	1.2040 ± 2	(.0001)	1.2022
γ_1	1.0963	+.0002	1.096038 ± 7	(.00002)	1.09516
γ_2	1.0655	.0000	1.06555 ± 4	(.0000)	1.06548
γ_3	1.0592	−.0004	1.05926 ± 3	(.0001)	1.05930
γ_4	1.0260	−.0001	1.02611 ± 6	(.0000)	1.02614

correct for or eliminate the sources of error mentioned above. In particular Siegbahn designed an interesting spectrometer for the express purpose of reducing the errors due to penetration of the X-rays into the crystal, etc., to a minimum.

Overn does not include the lines l and η in his table of wave lengths. He suggests, however, that the marks on photographic plates corresponding to η may represent the α_1 line in the K series of molybdenum in the second order spectrum. As the lines l and η are of considerable theoretical importance we have tested this point by examining the spectrum in the neighborhood of $K\alpha_1$ for molybdenum in the first order spectrum. We found evidence for both molybdenum $K\alpha_1$ and $K\alpha_2$, but their intensities were less than that of the line we regard as $L\eta$ of tungsten. As the intensity of the second order spectrum is very much less than that of the first order spectrum it is impossible that the peak on our curve should represent molybdenum $K\alpha_1$ in the second order.

Critical Absorption Wave-Lengths.—In general the measurement of critical absorption wave-lengths is more difficult and slightly less accurate than that of emission lines. In order to make such a measurement we usually place a screen containing the chemical element to be investigated

in the path of the incident beam of rays between the X-ray tube and the spectrometer, take a series of readings in the neighborhood of the critical point and draw the corresponding ionization current crystal table angle graphs. Figs. 5, 6 and 7 contain such graphs. Owing to the fact that the absorbing substance absorbs X-rays of longer wave-length than the critical wave-length to a less extent than it does X-rays of shorter wave-length a sharp drop in the curve occurs at the critical point.

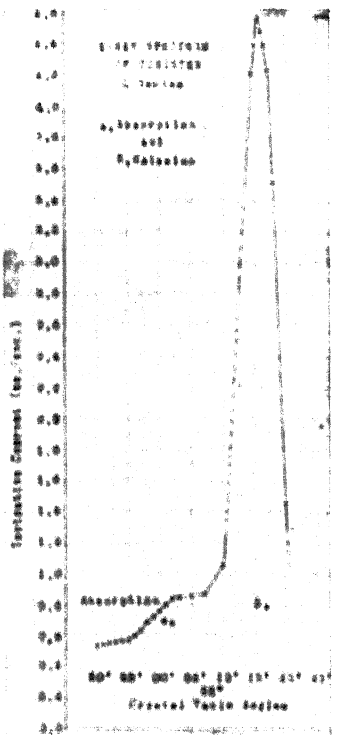


Fig. 8.

In Fig. 5 the absorption drop is due to the target itself, which was so placed that the beam of X-rays that struck the crystal left the target almost grazing its surface. Under these conditions the target absorbs a large part of its own radiation. Fig. 5 clearly shows the relative magnitudes of the emission and absorption spectra. The absorption drop is the largest of the three critical absorptions that have so far been observed in the L series of X-rays. The glancing angle, θ_{a1}, in this case has been estimated by taking the difference between it and the glancing angle, θ_{a2}, of the neighboring emission line.

The other two absorption drops fall so close to emission peaks that good measurements of them can not be made without using an X-ray tube with a target of a different chemical element. Professor D. L. Webster kindly loaned us such a tube, with a molybdenum target. Using it we obtained the curves, represented in Figs. 6 and 7, on both sides of the zero. We estimated the grazing angles, θ_{a2} and θ_{a3}, by measuring from the centers of the corresponding drops.

Fig. 7 contains curves for the K critical absorption of tungsten, obtained in the first, second and third order spectra. We are indebted to Dr. Stenstrom for his assistance in making these K series measurements.

Table III. contains the glancing angles and computed wave-lengths for the K and L characteristic absorption lines of tungsten.

We wish to call attention to the relative magnitudes of the critical absorption wave-lengths and the wave-lengths of the emission lines.

Tungsten Absorption Spectrum.

K and L Critical Absorption Wave-Lengths.

Grating Constant for Calcite $2d = 6.056 \times 10^{-8}$ cm.

Absorption.	Order.	Glancing Angle, θ.	Wave-length, $\lambda \times 10^{8}$ Cm.
$K\alpha$.....	1	1°-41'-15"	0.17813
$K\alpha$.....	2	3°-22'-19"	0.17810
$K\alpha$.....	3	5°-03'-20"	0.17789
			Weighted mean, 0.17806 ± 7
$L\alpha_1$.....	1	11°-33'-37"	1.2136 ± 1
$L\alpha_2$.....	1	10°-12'-07"	1.0726 ± 5
$L\alpha_3$.....	1	9°-44'-05"	1.024 ± 3

The critical absorption wave-length L_{α_1} is about 2¾ per cent. shorter than that of the β_2 emission line and about .8 of a per cent. longer than

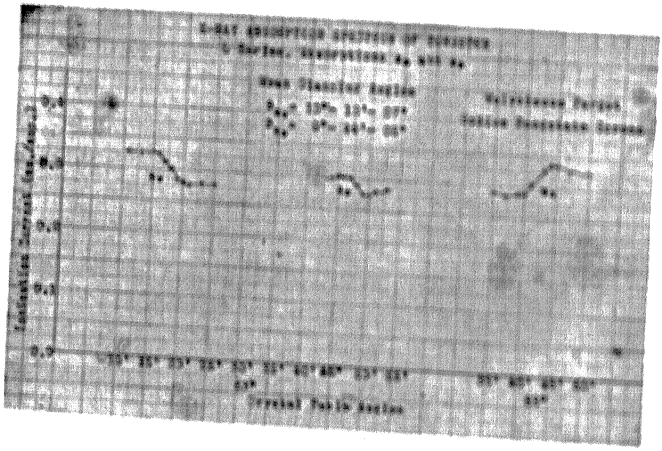


Fig. 6.

that of the β_5 emission line. $L\alpha_1$ lies in the midst of a number of faint lines that have been observed on photographic plates by Dershem, Overn and Siegbahn. $L\alpha_2$ lies between γ_1 and γ_2 (about 0.7 per cent. from γ_2). $L\alpha_3$ lies within a fraction of one per cent. of γ_4, and apparently on its short wave-length side.

Many of the general laws and theoretical equations relating to X-ray spectra are expressed in terms of the frequencies of vibration, the wave-numbers or the ratios of the frequencies to the fundamental Rydberg frequency for heavy atoms. The following table contains the values of ν/ν_∞ calculated from our data. In making these calculations we have used Paschen's value for the wave-number, ν_∞, namely $\nu_\infty = 109{,}737.11 \pm 0.06$, the accuracy of which far exceeds that of any X-ray measurement that can be made at the present time.

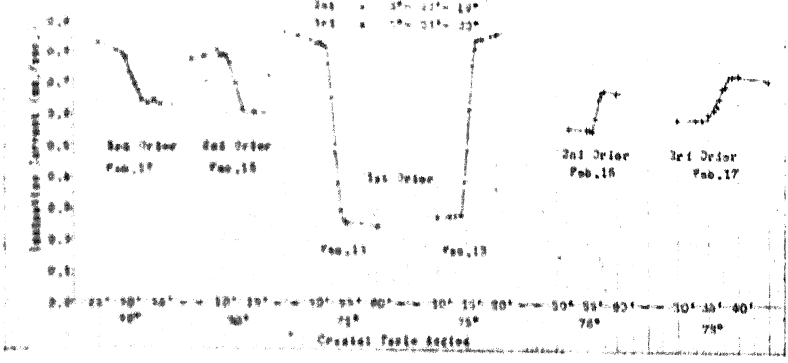


Fig. 7.

Table IV.

Tungsten X-Ray Spectrum.

Values of ν/R, for the K and L Critical Absorption and Emission Lines.

Critical Absorption	K 5118 ± .2	L_3 750.88 ± .07	L_{β_1} 849.6 ± .4	L_{α_3} 890. ± 3.	
K Series Emission	K_{α_2} 1750.6 ± .6	K_{α_1} 1768.4 ± .6	$K\beta$ 4947.2 ± .8	$K\gamma$ 5091. ± .2	
L Series Emission	l 844.9 ± .4	$L\alpha_2$ 614.10 ± .12	$L\alpha_1$ 618.62 ± .05	$L\eta$ 642.9 ± .3	
L Series Emission	$L\beta_4$ 701.8 ± .2	$L\beta_2$ 712.84 ± .05	$L\beta_5$ 724.17 ± .18	$L\beta_3$ 733.75 ± .07	$L\beta_6$ 756.9 ± .4
L Series Emission	$L\gamma_3$ 841.59 ± .06	$L\gamma_2$ 853.4 ± .4	$L\gamma_4$ 860.0 ± .3	$L\gamma_1$ 888.1 ± .5	

In the Physical Review for July, 1919, Duane and Shimizu published an account of experiments which showed that each of the α emission frequencies in the K series equaled the difference between the K critical absorption frequency and one of the L critical absorption frequencies. Theoretically this should be true provided that all the atoms (of the same chemical element) are exactly alike, *i.e.*, have the same kinds of orbits (for, if W and W' represent the amounts of energy in an atom of

[1] The values for the K series emission lines are taken from a paper by Duane and Stenström, presented to the Physical Society in February, 1920. See the Physical Review, April, 1920, p. 198.

quency is given by the equation

$$h\mathrm{K}\alpha = W_1 - W_2 \qquad (1)$$

Similarly, if W_2 represents the energy of the system when one of the electrons has been removed from an L orbit, the corresponding L critical absorption frequency is given by the equation

$$h\mathrm{L}\alpha = W_2 - W_3 \qquad (2)$$

According to the theory a Ka characteristic X ray is emitted when an electron falls from the $L\alpha$ orbit to the $K\alpha$ orbit, and during this transfer the energy of the atom changes from W_1 to W_2. The difference between these amounts of energy is radiated at a frequency $K\alpha$ given by the equation

$$h\mathrm{K}\alpha = W_1 - W_2 \qquad (3)$$

From equations (1), (2) and (3)

$$\mathrm{K}\alpha = \mathrm{K}\alpha - \mathrm{L}\alpha \qquad (4)$$

And this is the relation found by experiment to hold within the limits of error.

If, however, some atoms contain circular orbits and others elliptic orbits, both $K\alpha$ and $L\alpha$ will have different values for the different kinds of atoms. In fact all critical absorption, critical ionization and emission lines will have complex structures. We have not been able to observe such a structure in the absorption drops for chemical elements of high atomic weight. Further the data obtained this year corroborate the results arrived at last year to within the limits of experimental errors. These errors are smaller than those of last year's measurements, for (*a*) the wave-lengths are averages of a larger number of individual determinations, (*b*) some of them were measured in spectra of higher orders and (*c*) the thin glass window in the X-ray tube allowed a larger amount of X-ray energy to emerge from the tube.

The following values taken from Table III, show the precision with which the Ka emission frequencies equal the differences between the critical absorption frequencies.

TABLE V.

Tungsten X-Ray Spectra. Values of ν/ν_0.

Critical Absorption	Emission Lines
$K\alpha - L\alpha_1 = 4366.9 \pm 2.1$	$K\alpha_1 = 4368.3 \pm .6$
$K\alpha - L\alpha_2 = 4268.2 \pm 2.4$	$K\alpha_2 = 4270.6 \pm .6$

It is impossible to test directly the above law as applied to the L and the M series, for the M critical absorption wave-lengths have not been measured for tungsten.

Theoretically,[1] however, if two emission lines in the L series are produced by electrons falling from the *same* outer orbit to the La_1 and La_2 orbits respectively, the difference between their frequencies should equal that between the two critical absorption frequencies (except for the possible small correction due to the complex structure of the lines as explained above). The difference between the two critical absorption frequencies is

$$La_2 - La_1 = 98.7 \pm .5.$$

Turning to the emission lines we find that the following three pairs have frequency differences that equal the difference between the two critical absorption frequencies to within the limits of experimental error:

$$L\eta - Ll = 99.0 \pm .6, \qquad L\beta_1 - La_2 = 98.4 \pm .2,$$

$$L\gamma_2 - L\beta_3 = 98.4 \pm .7.$$

This would seem to indicate that the electrons producing the two lines in a pair fall from the same outer orbit. For instance we may suppose that La_2 and $L\beta_3$ are due to electrons falling from one of the M orbits. Measurements of the absorption frequencies for thorium and uranium which the authors presented to the Physical Society in April agree very well with this hypothesis. Further we may assume that Ll and $L\eta$ are produced by electrons falling from an orbit between the L and the M orbits. This orbit, however, has not been identified by means of a critical absorption frequency in the case of any chemical element. On the other hand there appears to be some difficulty in the theoretical interpretation in the case of the third pair, for the frequencies of the emission lines $L\beta_4$ and $L\gamma_3$ are greater than those of the critical absorption frequencies La_1 and La_2 respectively.

The difference between the frequencies of a fourth pair of emission lines is almost, but not quite equal to that between the critical absorption frequencies, namely

$$L\gamma_1 - L\beta_2 = 97.5 \pm .1.$$

It would seem that in this case the electrons producing the lines did not come from exactly the same outer orbit.

Siegbahn[2] finds that the difference in frequency between the lines in these pairs decreases slightly as the frequency itself increases.

[1] Compare an interesting discussion of this subject by A. Sommerfeld in Atombau und Spektrallinien, Chapter 4.

[2] Phil. Mag., Nov., 1919.

orbits. Making the relativity correction for the change of mass of a
electron with its velocity he finds that the energy of an electron travelling
in an elliptic orbit differs somewhat from that of the electron in the
corresponding circular orbit. This means that those atoms which have
elliptic L orbits produce spectra that differ in frequency from the spectra
of atoms with circular L orbits. Sommerfeld's equation for this differ-
ence $\Delta\nu$ in frequency (divided by ν_∞) reduces to

$$\frac{\Delta\nu}{\nu_\infty} = \frac{1}{\alpha^2}\left(\frac{N_2}{N_1} + \frac{N_1}{N_4} - \frac{N_2}{N_4}\right),$$

for the L series. In this equation

$$\alpha = \frac{2\pi e^2}{hc} = 7.295 \times 10^{-3}, \quad \text{and} \quad N_4 = \alpha N - n,$$

where e = the electron's charge, h = Planck's constant and c = the velocity of light.

The function representing the frequency difference, varies roughly as the fourth power of the atomic number, N, of the chemical element. It contains an arbitrary constant, n, the value of which he deduces from the wave-lengths in the X-ray spectra of a great many chemical elements. This value is $n = 3.63$. Putting it and $N = 74$ (for tungsten) in the formula we get 97.9 for the value of $\Delta\nu/\nu_\infty$ which agrees very well with our experimental results.

Sommerfeld recognizes the difficulty of giving a satisfactory physical interpretation to the above value of n (l. c.). Further it is worth noting that the formula does not take into account the changes in the energy of the other electrons in the atom when one of them is removed. These energy changes for the other electrons in the L orbit itself do not appear to be negligible, although, of course only the differences between their values for elliptic and circular orbits would enter into the equation.

HARVARD UNIVERSITY.

THE THERMO ELECTRIC EQUATION $P = TdV/dT$ ONCE MORE

By Edwin H. Hall

Jefferson Physical Laboratory, Harvard University

Communicated, March 27, 1919

At the Philadelphia meeting of the Academy in November, 1917, I questioned the validity of this equation as commonly understood, P being taken as the ordinary Peltier effect and V the Volta effect between any two metals. But I did not make my point of objection entirely clear and wish now to try again, for the matter is important.

It appears that Kelvin, who derived this equation from a course of theoretical reasoning, did not regard P as necessarily the Peltier effect only, believing that it might include some other, hitherto unknown, reversible heat effect accompanying movement of electric charge from one metal to another. O. W. Richardson, arriving at the same equation by a different course of reasoning, held P to be simply the Peltier effect. My colleague Professor Bridgman, repeating with some modifications of his own the argument of Kelvin and also that of Richardson, came at first to a conclusion sustaining that of Richardson, and submitted his unpublished paper to me for criticism.

I maintained that Kelvin's broader interpretation of the P was probably the correct one and ventured the suggestion that ionization and re-association within the metals according to the mass-law of equilibrium between free electrons and metal ions, furnished the reversible heat effect, additional to the ordinary Peltier effect, that Kelvin saw the need of. Bridgman felt, however, that I had not disposed of Richardson's argument, and accordingly I wish now to revise, but not to withdraw, my criticism.

The passage which I quoted from p. 28 of his *Emission of Electricity from Hot Bodies* ended with the equation

$$dS = \frac{1}{T}[d(nv\phi) + pdv],$$

in which dS is change of entropy of the system and "φ is the change in the energy of the system which accompanies the transference of each electron

jecting to this particular passage, for just here Richardson is speaking of an insulated piece of metal which is imagined to give off electrons that do work as a gas on a moving piston, and for such a 'virtual' operation his statement is doubtless true. But in his *experiments* he is really taking off a stream of electrons in the gas state from the metal, and an equal stream is constantly entering the metal by conduction, yet he assumes that the same Φ which occurs in the equation above quoted, for his case of virtual emission from an insulated body, holds as the heat of emission for his actual case.

It was this actual case, of electric flow, that I had in mind when I offered my criticism that his equation for dS fails when not only heat but substance also, that of the incoming electrons, is added to the system during the operation under consideration. I believe that this objection holds.

Bridgman, missing my point through my lack of precision in stating it, studied Richardson's argument again and presently made for himself the same discovery that I had made, so that he and I are now in agreement regarding the inaccuracy of Richardson's reasoning. He finds, moreover, that, when this inaccuracy is corrected, Richardson's line of argument leads to precisely the same result as Kelvin's.

Accordingly Bridgman now writes P'' instead of P' in the equation in question, meaning by P'' the total reversible heat effect that accompanies a virtual movement of charge from one plate to another of a condenser made of different metals, though he may not subscribe entirely to my theory as to the action of ionization and re-association within the metals.

I hope that Professor Bridgman's paper, dealing with thermo-electricity in a broad way, will be published before long.

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Vol. 6, pp. 149–154, March, 1920

INFERENCES FROM THE HYPOTHESIS OF DUAL ELECTRIC CONDUCTION: THE THOMSON EFFECT

By Edwin H. Hall

Jefferson Physical Laboratory, Harvard University

Communicated January 29, 1920

At the Washington meeting of the National Academy of Sciences in April, 1919, I presented two papers that have not yet been published. One was on the *Effect of Pressure on Electric Resistance and on Peltier Heat in Metals*, the other on *Thermal Conduction in Metals*, both being written from the standpoint of Dual Electric Conduction.

The first named of these two papers contained implicitly the following propositions:

1*a*. Increase of pressure should, by bringing the atoms and the metal ions closer together, increase k_a, the associated-electron conductivity, and decrease k_f, the free-electron conductivity. We might, then, expect the total conductivity, k, to increase under pressure in metals having a relatively small value of $(k_f \div k_a)$ and to decrease in metals having a relatively large value of this ratio.

1*b*. As antimony and bismuth have exceptionally small values of k, they probably have exceptionally large values of $(k_f \div k_a)$, and this may account for the fact that, among twenty metals examined by Bridgman, these two were the only ones to show a decrease of conductivity under an increase of pressure.

2*a*. If the ratio $(k_f \div k_a)$ is greater in metal B than in metal A, ionization must occur at the junction of the two metals when a current flows from A to B, and re-association must occur there when the current flows from B to A. As ionization is doubtless accompanied by absorption of heat and re-association by evolution of heat, we have here an action which may play a very important part, if not the chief part, in the Peltier effect.

2*b*. The exceptionally large value of $(k_f \div k_a)$ that probably exists in bismuth may account for the fact that heat is absorbed when a negative current goes into this metal from any other.

2*c*. As increase of pressure probably decreases the ratio $(k_f \div k_a)$, we should expect an absorption of heat where a negative current flows from a metal under high pressure to the same metal uncompressed. If we call this effect of compression *plus* and the opposite effect *minus*, we

but five showed mixed effects, *minus* at 0° C. and *plus* at 100° C.

3*a*. According to the theory under discussion the Thomson effect should disappear if $(k_f \div k_a)$ became zero. Accordingly increase of pressure, causing a decrease of this ratio, should diminish the Thomson effect. Among eighteen metals examined by Bridgman under pressure, nine showed a decrease throughout the whole range of observation, one showed an increase through the whole range of observation, one showed zero change everywhere, the other seven showed mixed effects.

The following may be taken as a summary of the second paper:

1. Thermal conduction in a metal may be due to the convective action of a circulating electric current, free electrons moving down the temperature gradient and associated electrons moving up, with ionization at the hot end of the metal, involving absorption of heat, and re-association at the cold end, involving the emission of heat.

2. A quantitative test of this thesis, made necessarily with various assumptions, indicated ionizing potentials of the same order of magnitude as those observed in the ionization of metal vapors; but it seemed doubtful whether values so large as those here indicated are consistent with the magnitudes of the Thomson effect. It is to be noted that ionization within the solid body of a metal may well require less energy than ionization of the vapor.

It seemed desirable to study the Thomson effect more fully from the standpoint of dual electric conduction before proceeding farther with the theory of thermal conduction. The results of an examination of the Thomson effect are now ready for publication.

THE THOMSON EFFECT

In what follows:

n = the no. of free electrons per cu. cm. of a metal.

v = the no. of cu. cm. of metal containing 1 gm. of free electrons.

m = mass of electron, and G = no. of electrons in 1 gm. of electrons.

Then $nv = G = 1 \div m$.

p = press. of free electrons, in dynes per sq. cm. of cross-section of the metal. (1)

R = the gas constant for one molecule, or for one electron, = 1.37×10^{-16}.

Then $p = nRT$,

and, for 1 gm. of free electrons, $pv = nvRT = RT \div m$. (2)

P = electro-mag. pot. due to purely electric forces within the metal. (3)

P_a = electro-mag. pot. due to differential attraction of the unequally heated metal for the associated electrons.

P_f = corres. pot. due to differential attraction of the metal for the free electrons.

k_a = part of specific electric conductivity due to associated electrons.
k_f = part of specific electric conductivity due to free electrons.
k = $k_a + k_f$ = total electric conductivity.
e = the electron charge in electro mag. measure = 1.6×10^{-20}.
λ = the latent heat of ionization per $(1 \div e)$ electrons, in ergs.
λ' = the latent heat of ionization per electron, in ergs.

Hypothesis (A) is, that the mere mechanical tendency of the free electrons is toward uniformity of pressure throughout the unequally heated metal.

Hypothesis (B), alternative with (A), is that the mechanical tendency of the free electrons is toward the state of equilibrium produced by thermal effusion; that is,

$$p \div T^{1/2} = \text{constant}. \qquad (4)$$

Let C of figure (1) be the cold end and H the hot end of a metal bar forming part of a circuit in which an electric current is maintained by thermo electric action, the resistance of some part of the circuit being so great that the conditions existing in CH are very little different from those of equilibrium. In this case the Joule heat generated in CH can be neglected in comparison with the Thomson heat there generated or absorbed.

Contrary to custom, the direction of the stream of electrons through the metal will, in this paper, be taken as the direction of the current, and accordingly σ, the Thomson heat at any temperature T, will be defined as the heat absorbed by the electromagnetic unit quantity of electricity, $(1 \div e)$ electrons, in going through the metal from a place of temperature $(T - 0.5)$ degree to a place of $(T + 0.5)$ degree. This definition will make σ negative for copper and positive for iron. The value of σ will be expressed in ergs.



FIG. 1

When the unit quantity of electricity, $(1 \div e)$ electrons, $(m \div e)$ gm., goes through the slice dl of the bar CH, from the isothermal surface T to the isothermal surface $T + dT$, the fraction $(k_f \div k)$ of it consists of free electrons and the part $(k_a \div k)$ of associated electrons. We have now to take note of the changes of energy, of various kinds, undergone by these two parts of the current. We shall list the various forms of energy here considered under five general heads: (1) bulk potential energy, or pv potential energy, to which the free electrons only are subject; (2) kinetic energy of the electrons, which we shall regard as negligible in the associated electrons and equal to that of monatomic gas molecules in the free electrons, (3) electric charge potential energy, the P energy, to which both the free and associated electrons are alike subject; (4) the P_f potential

the associated electrons only. We must take account also of the gain of energy involved in the ionization which may occur in the current from T to $T + dT$, due to the increase in the ratio $(k_f + k)$ with rise of temperature.

Under hypothesis (A): All changes due to change of $(k_f + k)$ being considered last, we have as the change of pv energy, (see equation (3))

$$(k_f + k)(m + e)d(pv) = (k_f + k)(R + e)dT. \tag{a}$$

The gain of thermal kinetic energy by the free electrons is

$$(k_f + k)(1 + e) \cdot \frac{3}{2} RdT. \tag{b}$$

The gain of P potential energy is dP. (c)

The gain of P_f potential energy is $(k_f + k)dP_f$. (d)

The gain of P_a potential energy is $(k_a + k)dP_a$ (e)

The gain of energy through ionization is

$$\lambda d(k_f + k) = (1 + e)\lambda' d(k_f + k). \tag{f}$$

The sum of all these quantities is the Thomson-effect heat absorbed between T and $T + dT$; that is

$$\sigma dT = (a) + (b) + (c) + (d) + (e) + (f) \tag{5}$$

From this we get

$$\sigma = \frac{k_f}{k} \cdot \frac{5}{2} \frac{R}{e} + \left[\frac{k_f}{k} \cdot \frac{dP_f}{dT} + \frac{k_a}{k} \cdot \frac{dP_a}{dT} + \frac{dP}{dT} \right] + \frac{\lambda'}{e} \cdot \frac{d(k_f + k)}{dT}. \tag{6}$$

From the conditions of equilibrium, under hypothesis (A), in a detached bar like CH we have[1]

$$\frac{k_f}{k} \cdot \frac{1}{e} \left(\mathrm{R} + \frac{RT}{n} \cdot \frac{dn}{dT} \right) + \left[\frac{k_f}{k} \cdot \frac{dP_f}{dT} + \frac{k_a}{k} \cdot \frac{dP_a}{dT} + \frac{dP}{dT} \right] = 0 \tag{7}$$

Subtracting (7) from (6) we get

$$\sigma = \frac{k_f}{k} \cdot \frac{3}{2} \frac{R}{e} - \frac{k_f}{k} \cdot \frac{RT}{ne} \cdot \frac{dn}{dT} + \frac{\lambda'}{e} \cdot \frac{d(k_f + k)}{dT}. \tag{8}$$

Under hypothesis (B) we get $0.5R$ instead of the first R in (7), and this gives $2R$ instead of $1.5R$ in the first term of (8). Hypothesis (B) makes no other change in (7) or (8).

I shall now try to put equation (8) into a form suitable for dealing with the values of σ found by Bridgman[2] in his experiments on a large number of metals. In this undertaking I assume that for present purposes the following equations hold above 0° centigrade:

$$n = sT^q, \tag{9}$$

and

$$(k_f + k) = C + C_1 t + C_2 t^2, \tag{10}$$

where s, q, C, C_1 and C_2 are constants, and t is temperature on the ordinary centigrade scale.

I shall, moreover, assuming that the total heat of ionization per electron is made up of a part λ'_o, due to the overcoming of atomic attraction, a part $1.5RT$ for the kinetic energy gained, and a part RT for the pv potential energy gained, write

$$\lambda' = \lambda'_o + 2.5RT = \lambda'_o + 2.5R(273 + t). \tag{11}$$

Keeping to hypothesis (A) and so using equation (8) for σ, I get by substitution according to eqs. (9), (10) and (11),

$$\sigma = K + (K_1 + K_2 t)T, \tag{12}$$

where K, K_1 and K_2 are constants,[3] defined by the equations

$$K = \frac{R}{c}\left[C(1.5 - q) + C_1\left(\frac{\lambda'_o}{R} - 273(1.5 - q)\right) - 273C_2\left(\frac{2\lambda'_o}{R} - 273(1.5 - q)\right)\right] \tag{13}$$

$$K_1 = \frac{R}{c}\left[C_1(4 - q) + C_2\left(\frac{2\lambda'_o}{R} - 273(1.5 - q)\right)\right] \tag{14}$$

$$K_2 = \frac{R}{c}\cdot C_2(0.5 - q). \tag{15}$$

I have put σ into the form shown by equation (12) in order to make my expression for it correspond as nearly as may be to that used by Bridgman to set forth the results of his experiments. He writes, in substance,

$$\sigma = (A + Bt)T, \tag{16}$$

where A and B are constants, the latter being zero in many metals.

Bridgman finds nothing corresponding to my constant K, and I have spent much labor in attempting to get rid of this constant; but no reasonable assumption that I can make eliminates it from my general expression for σ. On the other hand, equation (13) shows that K is the sum of many terms, some positive, some negative, and there is nothing to show that it may not be very small, too small to appear in such experiments as those of Bridgman. Accordingly, in dealing with his observations I put K, and so the second member of (13), equal to zero. This gives me an equation of which I make frequent use in the form

$$C = \left[C_1\left(\frac{\lambda'_o}{R} - 273(1.5 - q)\right) + 273C_2\left(\frac{2\lambda'_o}{R} - 273(1.5 - q)\right)\right] \div (1.5 - q). \tag{17}$$

As to the A and B of equation (16), I take these to be, respectively, the K_1 and the K_2 of my equations, and, as Bridgman gives the value of A and B for every case dealt with, I have the K, K_1 and K_2, of equations (13), (14) and (15), replaced by definite numerical terms.

These three equations now contain the five unknowns, C, C_1, C_2, λ'_o, and q. Accordingly, I must assume values for two of these quantities in order to evaluate the other three. As a rule, I have assumed values of

out the corresponding values of the other quantities, including the order C_2, C_1, C.

Values of q and λ'_0 that would lead to values for C greater than 1 or less than 0 are of course rejected, as such values of C would be meaningless, but negative values of C_2 and C_1 are not to be regarded as impossible. I was at first inclined to the opinion that the ratio $K_2 : K$ would always increase with rise of temperature, but this is not a logical necessity, in the present state of our knowledge, and it appears from what follows that the ratio in question is quite as likely to decrease as to increase in the temperature ascent from 0° to 100°. An interesting relation between this conclusion and the observations of Bridgman on change of resistance under pressure, at various temperatures, will be shown in this paper.

Cases in which K_2, or B, is 0. In twelve of the seventeen metals for which Bridgman gives the value of α the B of equation (16) is zero. Such cases are very easy to deal with. We have $K_2 = 0$, and so, from equation (15), $C_2 = 0$, unless q has the improbably large value 0.5. If C_2 is 0, we have, from equation (14),

$$C_1 = K_1 \text{ (or } A) \frac{e}{R} + (4 - q) \tag{18}$$

Substituting for C_1 in equation (17), we get

$$C = \left[-K_1 \cdot \frac{e}{R}\left(\frac{\lambda'_0}{R} - 273(1.5 - q)\right) + (4 - q)\right] + (1.5 - q) \tag{19}$$

For any given value of q this becomes

$$C = K'\lambda'_0 - K'' \tag{20}$$

where K' and K'' are new constants, the values of which depend on q.

This equation shows that, for a fixed value of q, we can represent the

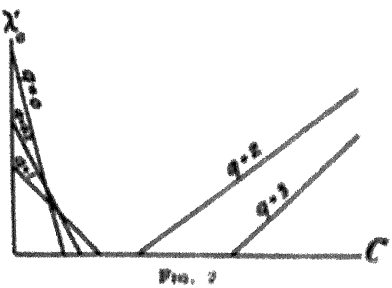


FIG. 2

relation of C to λ'_0 by means of a straight line drawn on the (C, λ'_0) plane. Such a line is useful for purposes of interpolation and extrapolation.

It is to be noted that the metals for which K_2 is 0 fall into two groups, for one of which K_1 is positive, while for the other it is negative.

Figure 2 shows the general character of the set of q-constant lines for the first group, and figure 3 does the same for the second group.

For both of these groups 1.5 is a critical value for q. Examination of equation (19) shows that, when $q = 1.5$, C becomes infinite unless λ'_0 at the same time becomes 0; and if λ'_0 becomes 0 while $q = 1.5$, C becomes

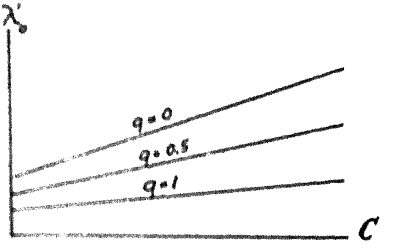


FIG. 3

indeterminate. In both figure 2 and figure 3, therefore, $q = 1.5$ would imply a line coincident with the C axis.

If q in equation (19) has a value between 1.5 and 4, C will have the same sign as K_2, which is positive for the first group and negative for the second group. Accordingly, since negative values of C are meaningless, $1.5 < q < 4$ is possible for the first group but not for the second group.

Cases in which K_2 is not 0. There are in Bridgman's list five metals for which K_2, or B, is not zero. These are aluminium, gold, iron, molybdenum, and thallium. Finding the value of C, for a given combination of q and λ'_0, in these metals, is a somewhat roundabout, though not difficult, process. The value of C_2 is found by use of equation (15), then the value of C_1 by use of (14), then the value of C by use of (17). The q-constant lines on the $(C\ \lambda'_0)$ plane are no longer straight, as they are in figures 2 and 3. Figure 4 shows their general shape for $q = 0$, $q = 0.5$ and $q = 1$, in the range from $C = 0$ to $C = 0.20$. It is to be noted that, though K_2 is positive in iron and thallium while negative in aluminium, gold,

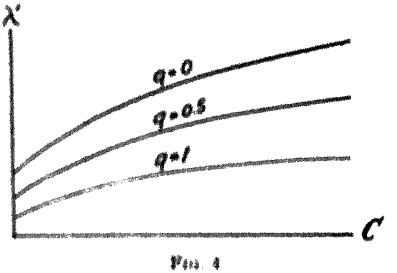


FIG. 4

and molybdenum, the lines in question are of the same general shape and arrangement for all five metals. The value of K_2 is positive for all.

Examination of equation (17) shows that, when $q = 1.5$, C is ∞ or is indeterminate. In the latter case, we may have either $\lambda'_0 = 0$ or $C_1 = 540C_2$.

When q is made larger than 1.5 but smaller than 6.0, negative values of C result, in all five of the metals, so far as I have examined the matter.

The following tables represent my results for all of the elementary metals for which Bridgman gave the values of σ in the paper already referred to. A dash (—) in place of a number indicates that the number would be negative, and that a negative value in this place is regarded as impossible.

The values of $(k_f + k)$ at 100° are found by use of equation (10).

The δ_0 of these tables is the "ionizing potential" needed for dealing with the attraction which an electron must overcome in the process of ionization. If this ionizing potential is 1 volt, for example, the *internal* work of ionization is about 11700 K ergs per electron. The *external* work of ionization, to provide the kinetic energy and the pv energy of the gaseous state, is 2.5 RT ergs per electron. This at 0° would require an ionizing potential of about 0.058 volt, which must be added to the δ_0 of the tables in order to get the total ionizing potential in volts.

The general significance of these tables can be illustrated as follows, with numbers taken from table 1. If in cobalt the value of C is 30%, the Thomson effect heat, as found by Bridgman for this metal, can be accounted for either by

taking $q = 2$, $\delta_0 = 0.02$, $C_1 = 457 \times 10^{-6}$, $C_2 = 0$,

or by

taking $q = 3$, $\delta_0 = 0.01$, $C_1 = 915 \times 10^{-6}$, $C_2 = 0$.

In the first case $(k_f + k)$ will be 0.346 at 100°, while in the second case it will be 0.392. If the value of C is 40%, there are corresponding values of q, δ_0, etc., that will account for σ. A like statement would hold for any value of C between 30% and 40%, and for numberless other values of this ratio.

First Group: Metals for which $K_1 > 0$ and $K_2 = 0$

TABLE 1. COBALT

$K_1 = 7.8$, $K_2 = 0$, $C_2 = 0$

C, or $(k_f + k)$, at 0°	$C_1 = 228 \times 10^{-6}$			$C_1 = 261 \times 10^{-6}$			$C_1 = 305 \times 10^{-6}$			$C_1 = 457 \times 10^{-6}$			$C_1 = 915 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.01	0	.03	.033	5	.02	.036	1	.01	.041	2			3		
0.08[1]	0	—		5	—		1	.00	.111	2			3		
0.20	0	—		5	—		1	—		2	.01	.246	3		
0.30	0	—		5	—		1	—		2	.02	.346	3	.01	.392
0.40	0	—		5	—		1			2	.03	.446	3	.02	.492

[1] If there is any combination of q and δ_0 that will make $C = 0.10$ for cobalt, the q must be very near 1.5.

TABLE 2. NICKEL.

$K_1 = 3.56,\ K_2 = 0,\ C_2 = 0$

C_1 at $(k_f + k)$ at 0°	$C_1 = 104 \times 10^{-6}$			$C_1 = 119 \times 10^{-6}$			$C_1 = 139 \times 10^{-6}$			$C_1 = 208 \times 10^{-6}$			$C_1 = 416 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.01	0	.02	.020	5	.016	.022	1	.01	.024	2	—		3	—	
0.10	0			5			1			2	.010	.121	3	—	
0.20	0			5			1			2	.033	.221	3	.03	.242
0.30	0			5			1			2	.056	.321	3	.06	.342
0.40	0			5			1			2	.079	.421	3	.09	.442

PALLADIUM

$K_1 = 3.52,\ K_2 = 0,\ C_2 = 0$

Palladium is so like nickel in its Thomson effect that table 2 will serve for it.

TABLE 3. PLATINUM.

$K_1 = 2.67,\ K_2 = 0,\ C_2 = 0$

C_1 at $(k_f + k)$ at 0°	$C_1 = 78 \times 10^{-6}$			$C_1 = 89 \times 10^{-6}$			$C_1 = 104 \times 10^{-6}$			$C_1 = 156 \times 10^{-6}$			$C_1 = 312 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.01	0	.02	.018	5	.01	.019	1	.01	0.20	2	—		3	—	
0.10	0			5			1			2	.02	.116	3	.01	.131
0.20	0			5			1			2	.05	.216	3	.05	.231
0.30	0			5			1			2	.08	.316	3	.09	.331
0.40	0			5			1			2	.11	.416	3	.13	.431

TABLE 4. TIN.

$K_1 = 0.134,\ K_2 = 0,\ C_2 = 0$

C_1 at $(k_f + k)$ at 0°	$C_1 = 192 \times 10^{-6}$			$C_1 = 448 \times 10^{-6}$			$C_1 = 520 \times 10^{-6}$			$C_1 = 780 \times 10^{-6}$			$C_1 = 1560 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.01	0			5			1			2	0.05	.011	3	0.05	.012
0.10	0			5			1			2	0.52	.101	3	0.79	.102
0.20	0			5			1			2	1.04	.201	3	1.62	.202
0.30	0			5			1			2	1.56	.301	3	2.45	.302
0.40	0			5			1			2	2.08	.401	3	3.28	.402

$K_2 = 0.00,\ K_3 = 0,\ C_3 = 0$

C_1 or $(kf+k)_1$ at 0°	$C_1 = 29 \times 10^{-4}$			$C_1 = 15 \times 10^{-4}$			$C_1 = 58 \times 10^{-4}$			$C_1 = 87 \times 10^{-4}$			$C_1 = 116 \times 10^{-4}$		
	q	k_0	$(kf+k)$ at 100°	q	k_0	$(kf+k)$ at 100°	ζ	k_1	$(kf+k)$ at 100°	ζ	k_1	$(kf+k)$ at 100°	ζ	k_1	$(kf+k)$ at 100°
0.01	0	—		5			1	0	014	2			3		
0.10	0	—		5			1			2	00	100	3	05	112
0.20	0	—		5			1			2	11	200	3	18	212
0.30	0	—		5			1			2	20	300	3	30	312
0.40	0	—		5			1			2	28	400	3	41	412

Second Group: Metals for which $K_2 < 0$ and $K_3 = 0$

TABLE 6. BISMUTH

$K_1 = -3.2,\ K_2 = 0,\ C_3 = 0$

C_1 or $(kf+k)_1$ at 0°	$C_1 = -94 \times 10^{-4}$			$C_1 = -[illegible] \times 10^{-4}$			$C_1 = -[illegible] \times 10^{-4}$		
	q	k_0	$(kf+k)$ at 100°	q	k_0	$(kf+k)$ at 100°	ζ	k_1	$(kf+k)$ at 100°
0.01	0	0.05	0.001	0.5	0.01	0.001	1	0.01	0.100
0.10	0	0.17	0.091	0.5	0.10	0.089	1	0.04	0.087
0.20	0	0.31	0.191	0.5	0.18	0.189	1	0.08	0.187
0.40	0	0.58	0.391	0.5	0.34	0.389	1	0.14	0.387
0.60	0	0.85	0.591	0.5	0.50	0.589	1	0.21	0.587

TABLE 7. CADMIUM

$K_1 = -32.4,\ K_2 = 0,\ C_3 = 0$

C_1 or $(kf+k)_1$ at 0°	$C_1 = -94 \times 10^{-4}$			$C_1 = -[illegible] \times 10^{-4}$			$C_1 = -[illegible] \times 10^{-4}$		
	q	k_0	$(kf+k)$ at 100°	q	k_0	$(kf+k)$ at 100°	ζ	k_1	$(kf+k)$ at 100°
0.01	0	0.036		0.5	0.024	—	1	0.012	—
0.10	0	0.049	0.006	0.5	0.032	—	1	0.015	—
0.20	0	0.062	0.106	0.5	0.040	0.093	1	0.019	0.075
0.40	0	0.090	0.306	0.5	0.055	0.293	1	0.026	0.275

TABLE 8. COPPER

$K_1 = -0.066,\ K_2 = 0,\ C_3 = 0$

C_1 or $(kf+k)_1$ at 0°	$C_1 = -28 \times 10^{-4}$			$C_1 = -15 \times 10^{-4}$			$C_1 = -58 \times 10^{-4}$		
	q	k_0	$(kf+k)$ at 100°	q	k_0	$(kf+k)$ at 100°	ζ	k_1	$(kf+k)$ at 100°
0.01	0	0.08	0.007	0.5	0.05	0.006	1	0.02	0.006
0.10	0	0.49	0.097	0.5	0.26	0.096	1	0.12	0.096
0.20	0	0.95	0.197	0.5	0.48	0.196	1	0.24	0.196
0.40	0	1.87	0.397	0.5	0.92	0.396	1	0.48	0.396

TABLE 9 MAGNESIUM[a]

$K_1 = -0.008$, $K_2 = 0$, $C_2 = 0$

C_1 at $(k_f + k)$ at 0°	$C_1 = -24 \times 10^{-6}$			$C_1 = -27 \times 10^{-6}$			$C_1 = -31 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.001	0	0.04	0.001	0.5	0.34	0.001	1	0.15	0.001
0.01	0	0.4	0.01	0.5	3.2	0.01	1	1.4	0.01
0.05	0	2.7	0.05	0.5	16.0	0.05	1	7.0	0.05

[a] The Thomson effect in magnesium was very small, and the values of δ_0 indicated for this metal are exceptionally large. Bridgman, however, describes the specimen used as of commercial quality, and thinks it was impure.

TABLE 10 SILVER

$K_1 = -0.804$, $K_2 = 0$, $C_2 = 0$

C_1 at $(k_f + k)$ at 0°	$C_1 = -27 \times 10^{-6}$			$C_1 = -29 \times 10^{-6}$			$C_1 = -34 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.01	0	0.09	0.007	0.5	0.05	0.007	1	0.02	0.007
0.10	0	0.54	0.097	0.5	0.32	0.097	1	0.14	0.097
0.20	0	1.04	0.197	0.5	0.61	0.197	1	0.26	0.197
0.40	0	2.04	0.397	0.5	1.19	0.397	1	0.50	0.397

TABLE 11 TUNGSTEN

$K_1 = -3.41$, $K_2 = 0$, $C_2 = 0$

C_1 at $(k_f + k)$ at 0°	$C_1 = -102 \times 10^{-6}$			$C_1 = -114 \times 10^{-6}$			$C_1 = -130 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.01	0	0.05	0.000	0.5	0.03	0.000	1	0.02	0.000
0.10	0	0.16	0.090	0.5	0.10	0.089	1	0.05	0.087
0.20	0	0.29	0.190	0.5	0.17	0.189	1	0.08	0.187
0.40	0	0.55	0.390	0.5	0.32	0.389	1	0.14	0.387

Third Group: Metals for which $K_1 < 0$ and $K_2 > 0$

TABLE 12 IRON

$K_1 = -1.78$, $K_2 = 0.0516$

C_v or $(k_f + k)$, at 100°	$C_v = 91 \times 10^{-6}$				$C_v = 100 \times 10^{-6}$				$C_v = 110 \times 10^{-6}$			
	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°
0.001	0	.015	66	017	5	010	50	018	1	005	77	020
0.01	0	.019	44	024	5	012	57	020	1	006	68	028
0.05	0	.031	−21	057	5	019	10	061	1	008	43	065
0.10	0	.042	−81	101	5	027	43	106	1	013	9	112
0.15	0	.052	−135	146	5	034	90	151	1	017	20	158
0.20	0	.060	−178	192	5	039	123	198	1	020	52	205
0.25	0	.068	−221	237	5	045	163	244	1	022	60	254

TABLE 13 THALLIUM

$K_1 = 0.268$, $K_2 = 0.00330$

C_v or $(k_f + k)$, at 0°	$C_v = 6 \times 10^{-6}$				$C_v = 6.5 \times 10^{-6}$				$C_v = 7.5 \times 10^{-6}$			
	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°
0.001	0	.020	7	002	5	010	10	003	1	006	10	003
0.01	0	.048	−3	011	5	034	1	011	1	016	5	011
0.05	0	.130	−32	047	5	090	25	048	1	050	14	049
0.10	0	.186	−51	096	5	130	42	096	1	080	31	098
0.15	0	.227	−65	144	5	160	55	145	1	096	40	147
0.20	0	.262	−78	193	5	186	66	194	1	105	45	196
0.30	0	.324	−99	291	5	220	81	293	1	135	62	295

Fourth Group: Metals for which $K_1 < 0$ and $K_2 < 0$

TABLE 14 ALUMINUM

$K_1 = -0.016$, $K_2 = 0.180$

C_v or $(k_f + k)$, at 0°	$C_v = 11 \times 10^{-6}$				$C_v = 12 \times 10^{-6}$				$C_v = 13 \times 10^{-6}$			
	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°	q	k_a	$C_v \times 10^{-6}$	$(k_f + k)$ at 100°
0.001	0	.020	−1	002	5	012	−1	002	1	006	1	002
0.01	0	.036	−11	010	5	022	−9	010	1	012	−7	011
0.05	0	.086	−41	047	5	058	−37	048	1	032	−30	048
0.10	0	.125	−64	095	5	088	−61	095	1	047	−46	097
0.20	0	.180	−97	191	5	120	−91	192	1	068	−69	194
0.30	0	.226	−125	289	5	155	−114	290	1	088	−91	292

TABLE 18. GOLD.

$K_1 = 0.934$, $K_2 = 0.001$

C_1 at $(k_f + k)$ at 0°	$C_1 = 1.8 \times 10^{-6}$				$C_1 = 3.0 \times 10^{-6}$				$C_2 = 2.1 \times 10^{-6}$			
	q	δ_0	$C_1 \times 10^{-6}$	$(k_f + k)$ at 100°	q	δ_0	$C_1 \times 10^{-6}$	$(k_f + k)$ at 100°	q	δ_0	$C_1 \times 10^{-6}$	$(k_f + k)$ at 100°
0.001	0	.032	29		5	.024	33		1	.011	—38	—
0.01	0	.051	31	.007	5	.040	35	.007	1	.018	—39	.006
0.05	0	.122	38	.046	5	.096	42	.046	1	.050	—44	.046
0.10	0	.188	45	.096	5	.158	50	.095	1	.083	—50	.095
0.20	0	.292	56	.195	5	.256	62	.194	1	.136	—58	.194
0.25	0	.334	60	.244	5	.294	77	.293	1	.158	—64	.244

TABLE 19. MOLYBDENUM.

$K_1 = 4.334$, $K_2 = 0.015$

C_1 at $(k_f + k)$ at 0°	$C_1 = 27 \times 10^{-6}$				$C_1 = 29 \times 10^{-6}$				$C_2 = 32 \times 10^{-6}$			
	q	δ_0	$C_1 \times 10^{-6}$	$(k_f + k)$ at 100°	q	δ_0	$C_1 \times 10^{-6}$	$(k_f + k)$ at 100°	q	δ_0	$C_1 \times 10^{-6}$	$(k_f + k)$ at 100°
0.001	0	.025	138		5	.017	155		1	.008	—175	
0.01	0	.030	146		5	.020	161		1	.010	—180	
0.05	0	.047	173	.035	5	.030	180	.035	1	.015	—192	.044
0.10	0	.064	197	.084	5	.042	204	.083	1	.020	—205	.083
0.20	0	.094	220	.181	5	.061	240	.179	1	.030	—230	.180

Comments

Lead does not appear in these tables, for the reason that σ for this metal is so small that we have no formula for it. Zero value for σ could be accounted for, according to the principles of this paper, in either of two ways:

First, as equation (8) shows, $(k_f + k)$ might be zero.

Second, if in equation (8) we make $(kf + k)$ a constant, of whatever value,[4] and is zero if $n \propto T$.[15]

These tables, like the experimental values of σ by means of which they are made, have no great pretension to accuracy. For example, it is doubtful whether much confidence can be placed in the small value of K_2, very nearly 0.001, found by Bridgman for gold. Yet the effect of neglecting this value is considerable. Thus, if we call $K_2 = 0$ for gold, we get

$K_1 = -0.934$, K_2 taken to be 0, and $C_2 = 0$

C_1, or $(k_f + k)$, at 0°	$C_1 = 27 \times 10^{-6}$			$C_1 = 13 \times 10^{-6}$			$C_1 = 76 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	z	δ_0	$(k_f + k)$ at 100°	z	δ_0	$(k_f + k)$ at 100°
0.01	0	0.08	0.007	0.5	0.05	0.007	1	0.02	0.006
0.10	0	0.51	0.097	0.5	0.30	0.097	1	0.14	0.096
0.20	0	0.99	0.197	0.5	0.58	0.197	1	0.25	0.196
0.40	0	1.95	0.397	0.5	1.14	0.397	1	0.49	0.396

Comparison of this with table 15 shows that ignoring the value of K_2, small as it is, makes a good deal of difference in the values of δ_0, though comparative little in the values of $(k_f + k)$ at 100°, as calculated by means of equation (10).

Uncertain as the values of $(k_f + k)$ are, there is little room for doubt in most cases, if my theory is substantially sound, as to the direction of change of these values when the temperature is raised. Accordingly I have divided all the metals represented by the preceding tables into two groups, in the first of which $(k_f + k)$ is greater at 100° than at 0°, while in the second group the ratio in question is greater at 0°.

For most of these metals Bridgman has determined the pressure coefficient of resistance at 0° and 100°. For magnesium the value at 0° only was found; for bismuth the highest temperature used was 75°. For all of the metals here considered except bismuth the coefficient in question is negative—that is, the resistance decreases with increase of pressure—but for bismuth it is positive. I shall make use of what Bridgman calls the *average* pressure-coefficient, the average value of the coefficient through a range of pressure from 0 kgm. to 12000 kgm. per square centimeter. I shall let π_0 represent the value of this coefficient at 0°, and π_{100} the value at 100°.

In accordance with what has been said in the opening paragraphs of this paper we should, other things being equal, expect π to decrease, numerically, with increase of $(k_f + k)$ in metals for which π is negative, and to increase with increase of $(k_f + k)$ in metals for which π is positive. Accordingly we might expect $(\pi_{100} - \pi_0) + \pi_0$ to be, in general, a negative quantity for metals in which $(k_f + k)$ increases with rise of temperature, and a positive quantity for metals in which $(k_f + k)$ decreases with rise of temperature—bismuth of course requiring exceptional consideration. The table given below enables us to test the validity of this expectation.

TABLE 17

(A)

METALS IN WHICH $k_f \div k$ INCREASES WITH RISE OF TEMPERATURE

	π_0	π_{100}	$(\pi_{100} - \pi_0) \div \pi_0$
Co	0.0$_5$873	0.0$_5$726	16.9%
Ni	0.0$_5$147	0.0$_5$138	+7.5%
Pd	0.0$_5$100	0.0$_5$186	2.1%
Pt	0.0$_5$187	0.0$_5$184	1.6%
Sr	0.0$_5$920	0.0$_5$951	+3.4%
Zn	0.0$_5$470	0.0$_5$454	3.4%
		Mean	2.2%

(B)

METALS IN WHICH $(k_f \div k)$ DECREASES WITH INCREASE OF TEMPERATURE

	π_0	π_{100}	$(\pi_{100} - \pi_0) \div \pi_0$
Ag	−0.0$_5$333	−0.0$_5$336	+0.9%
Al	−0.0$_5$382	−0.0$_5$377	−1.3%
Au	−0.0$_5$287	−0.0$_5$292	+1.7%
Bi[1]	+0.0$_4$223	+0.0$_4$202	+9.4%
Cd	−0.0$_5$894	−0.0$_5$927	+3.7%
Cu	−0.0$_5$183	−0.0$_5$177	−3.3%
Mg[2]	−0.0$_5$55		
Mo	−0.0$_5$129	−0.0$_5$127	−1.6%
Ta	−0.0$_5$115	−0.0$_5$123	+7.0%
W	−0.0$_5$123	−0.0$_5$126	+2.4%
			Mean +2.1%

[1] For bismuth, because π is positive and the highest temperature for π was 75°, we use $(\pi_0 - \pi_{75}) \div \pi_0$.

[2] Bridgman did not find π_{100} for magnesium.

Iron does not appear in this table, for the reason that, as table 12 shows, it should go into Section (*A*) under some conditions, but into Section (*B*) under other conditions. Its value of $(\pi_{100} - \pi_0) \div \pi_0$ is about 4%. This value, if put into Section (*A*), would make the mean value there −1.3%; put into Section (*B*), it would make the mean there +2.3%. If $(k_f \div k)$ for iron is greater than 10% at 0°C., which seems likely, iron belongs to Section (*B*).

Thallium and aluminium should go into Section (*A*) if $(k_f \div k)$ in them is less than 1% at 0°C., but this is improbable.

It is to be observed that for each section of table 17 the average value of $(\pi_{100} - \pi_0) \div \pi_0$ comes out with the sign it should have according to the predictions of the dual theory of electric conduction, as used in this paper, a *minus* sign for Section (*A*) and a *plus* sign for Section (*B*). This can hardly be pure accident.

Under Hypothesis (B)

All of the equations and all the tables of this paper, thus far, are based upon or are consistent with "hypothesis (*A*)." If hypothesis (*B*) is adopted instead, equation (8) is changed in the manner already described and the result in equations (13) to (19) is to replace 1.5 by 2, 4 by 4.5, and 6.5 by 7, in the parenthesis $(1.5 - q)$, $(4 - q)$ and $(6.5 - q)$.

The resulting tables, for cobalt and bismuth, the only metals for which the calculation has been made, are given in Tables 18 and 19 (below).

By comparison of these two tables with the corresponding ones obtained by the use of hypothesis (*A*) we see that no radical difference in the re-

pothesis (*B*) seems to give [illegible] somewhat larger values of k_2 than hypothesis [illegible]

TABLE [illegible]

$K = [illegible]$ $K_1 = [illegible]$ $\epsilon_1 = [illegible]$

C_1 or $(k_1 + k)$ at 0°	$\epsilon_1 = 202 \times 10^{-6}$											$\epsilon_1 = [illegible] \times 10^{-6}$
	θ	k_2	$k_2 + k$ at 100°	ϵ	λ	$\frac{k}{k_2}$	$\frac{k}{k_2}\epsilon$	λ	$\frac{k}{k_2}$	$\frac{k}{k_2}\epsilon$	λ	$\frac{k_2 + k}{k}$ at 100°
0 01	0	0038	0110	0 5	0279	0335		0279	0335	1 5	0335	040
0 05	0	004	0120	0 5	0267	0320		0267	0320	1 5	0385	080
0 10	0	—	—	0 5						1 5		

C_1 or $(k_1 + k)$ at 0°	$\epsilon_1 = 811 \times 10^{-6}$						$\epsilon_1 = [illegible] \times 10^{-6}$
	θ	k_2	$\frac{k_2 + k}{k}$ at 100°	ϵ	λ	$\frac{k}{k_2}\epsilon$	$\frac{k_2 + k}{k}$ at 0°
0 10	2 5			5			
0 15	2 5	0 002	0 190	5			
0 20	2 5	0 007	0 240	5	0 [illegible]	0 [illegible]	
0 30	2 5	0 016	0 340	5	0 [illegible]	0 [illegible]	
0 40	2 5	0 026	0 440	5	0 [illegible]	0 [illegible]	

TABLE [illegible]

$K_1 = [illegible]$ $K_2 = [illegible]$ $\epsilon_1 = [illegible]$

C_1 or $(k_1 + k)$ at 0°	$\epsilon_1 = 61 \times 10^{-6}$						$\epsilon_1 = [illegible] \times 10^{-6}$		
	θ	k_2	$\frac{k_2 + k}{k}$ at 100°	ϵ	λ	$\frac{k_2 + k}{k}$	ϵ	λ	$\frac{k_2 + k}{k}$ at 100°
0 01	0	0 07	0 002	0 5	0 05	0 003	1 5	0 03	0 000
0 10	0	0 25	0 002	0 5	0 17	0 001	1 5	0 10	0 000
0 20	0	0 46	0 102	0 5	0 32	0 [illegible]	1 5	0 [illegible]	0 [illegible]
0 40	0	0 87	0 302	0 5	0 58	0 [illegible]	1 5	0 [illegible]	0 [illegible]
0 60	0	1 26	0 502	0 5	0 84	0 [illegible]	1 5	0 [illegible]	0 [illegible]

In a paper already well advanced I shall undertake to show how far the data obtained in the present paper enable us to go in the way of explaining thermal conduction in the metals here dealt with.

[1] Eq. (7) is obtained from eq. (1) of my paper in the *Proceedings of the National Academy of Sciences* for April, 1918, by substituting for ϵ from eq. 2 of that paper (which equation should have s instead of m) and then making obvious changes.

[2] *Proceedings of the Amer. Acad. of Sciences*, Vol. 53, No. 4, 1918, pp. 269–306. These values are not regarded by Bridgman as accurate, having been obtained as second derivatives of e. m. f. values, the quantities measured, but taken as a whole they seem to be the best available data for the present purpose.

[3] This assumes that k'_1 is constant.

[4] When $(k_1 + k)$ is infinite, we have the conditions discussed in my paper "Thermo-electric Diagrams on the P-V Plane," *Proc. Amer. Acad. Boston*, February, 1918.

THE THOMSON EFFECT AND THERMAL CONDUCTION IN METALS

By Edwin H. Hall

Jefferson Physical Laboratory, Harvard University

Communicated July 14, 1920

The Thomson Effect. — In these PROCEEDINGS for March, 1920, is a paper in which I undertook to account for the Thomson effect values, as found by Bridgman for many metals, in accordance with the hypothesis of dual electric conduction.

Using data obtained by the methods of that paper, I was able, as I stated at the Washington meeting of the National Academy in April, 1920, to account quantitatively for the values of thermal conductivity found in a large number of metals at room temperature. I stated further, however, that the temperature coefficient of thermal conductivity indicated by my calculations was far too large to accord with the obvious facts, and that a revision of my formulae was therefore necessary. This revision, which has now been made, enables me to deal pretty satisfactorily with thermal conduction if my assumptions are granted. It involves important changes in most of the numerical tables in the paper referred to, but no great change in the method there followed.

The revision begins with equation (11), which is changed by the substitution of s for 2.5, so that it now stands

$$\lambda' = \lambda'_0 + sRT, \qquad (1)$$

where s is a constant, which varies from one metal to another but is always greater than 2.5. The λ' of this equation is the number of ergs required to separate one electron from its atomic union and leave it free, as a gas particle, within a metal, λ'_0 is a constant which may be different in different metals, and R is the gas constant for a single molecule. The assumption involved in this equation, like some others I have made, may seem improbable, but, as it does not, so far as I am aware, conflict with established facts or principles,[1] and as it serves my purpose fairly well, I have felt justified in adopting it provisionally.

As the total energy which a free electron possesses in virtue of its character as a monatomic gas molecule is $2.5\,RT$, the kinetic energy and the $p\upsilon$ energy being taken together, and as I assume that this energy is acquired in the act of ionization, I have

$$\lambda' = 2.5\,RT, \text{ or } \lambda'_0 + (s - 2.5)RT,$$

as the number of ergs required for overcoming the attractions or repulsions which are operative in the act of freeing a single electron from an atom, under the conditions which prevail within a solid metal. The

pothesis (B) seems to give, other things being equal, somewhat larger values of δ_0 than hypothesis (A).

TABLE 14 — COPPER

$K = 7.8$, $K_1 = 0$, $C_1 = 0$

C, or $(k_f + k)$, at 0°	$C_1 = 202 \times 10^{-6}$			$C_1 = 230 \times 10^{-6}$			$C_1 = 60 \times 10^{-6}$			$C_1 = 3.5 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.01	0	0.038	0.030	0.5	0.029	0.033	0.20	0.016	0.036	1.5	0.010	0.040
0.05	0	0.004	0.070	0.5	0.007	0.073	0.02	0.006	0.076	1.5	0.005	0.080
0.10	0	-		0.5						1.5		

C, or $(k_f + k)$, at 0°	$C_1 = 433 \times 10^{-6}$			$C_1 = 0.07 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.10	2.5			3		
0.15	2.5	0.002	0.190	3		
0.20	2.5	0.007	0.246	3	0.005	0.261
0.30	2.5	0.016	0.346	3	0.010	0.361
0.40	2.5	0.026	0.446	3	0.015	0.461

TABLE 15 — BISMUTH

$K_1 = -3.2$, $K_1 = 0$, $C_1 = 0$

C, or $(k_f + k)$, at 0°	$C_1 = 83 \times 10^{-6}$			$C_1 = 23 \times 10^{-6}$			$C_1 = 3.6 \times 10^{-6}$		
	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°	q	δ_0	$(k_f + k)$ at 100°
0.01	0	0.07	0.002	0.5	0.05	0.001	1.5	0.03	0.000
0.10	0	0.25	0.002	0.5	0.17	0.001	1.5	0.10	0.000
0.20	0	0.46	0.102	0.5	0.32	0.101	1.5	0.18	0.100
0.40	0	0.87	0.302	0.5	0.58	0.301	1.5	0.34	0.300
0.60	0	1.28	0.502	0.5	0.84	0.501	1.5	0.50	0.500

In a paper already well advanced I shall undertake to show how far the data obtained in the present paper enable us to go in the way of explaining thermal conduction in the metals here dealt with.

[1] Eq. (7) is obtained from eq. (1) of my paper in the *Proceedings of the National Academy of Sciences* for April, 1918, by substituting for ρ from eq. (2) of that paper (which equation should have n instead of m) and then making obvious changes.

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The revision begins with equation (11), which is changed by the substitution of s for 2.5, so that it now stands

$$\lambda' = \lambda'_0 + sRT, \qquad (1)$$

where s is a constant, which varies from one metal to another but is always greater than 2.5. The λ' of this equation is the number of ergs required to separate one electron from its atomic union and leave it free, as a gas particle, within a metal, λ'_0 is a constant which may be different in different metals, and R is the gas constant for a single molecule. The assumption involved in this equation, like some others I have made, may seem improbable, but, as it does not, so far as I am aware, conflict with established facts or principles,[1] and as it serves my purpose fairly well, I have felt justified in adopting it provisionally.

As the total energy which a free electron possesses in virtue of its character as a monatomic gas molecule is $2.5\,RT$, the kinetic energy and the $p\upsilon$ energy being taken together, and as I assume that this energy is acquired in the act of ionization, I have

$$\lambda' = 2.5\,RT, \text{ or } \lambda'_0 + (s - 2.5)RT,$$

as the number of ergs required for overcoming the attractions or repulsions which are operative in the act of freeing a single electron from an atom, under the conditions which prevail within a solid metal. The

supposed increase of this quantity with rise of temperature may be due to the expansion of the metal.

The meaning of P_0 and P_∞ symbols which I have used before and shall presently use again, is such that

$$P_f = P_\infty + \frac{1}{e}(\lambda' - \lambda) \qquad (2)$$

where e is the electron charge.

The revision leaves equations (13), (13'), (14) of my previous paper unchanged, but in (14) it substitutes $(6.5 - q)$ for $(4 - q)$ in the first term of the second member, and in (15) it puts $(2 + 1.5 - q)$ in place of $(6.5 - q)$.

Thermal Conduction. In December, 1917, I proposed[1] the following theory: That thermal conduction in a metal is due to the convective action of a circulating electric current, free electrons moving down the temperature gradient and associated electrons moving up, with ionization at the hot part of the metal, involving absorption of heat, and reassociation at the cold end, involving the emission of heat. I now propose to go as far as I can at present in the way of submitting this theory to a quantitative test.

As in my previous papers, "hypothesis (A)" will mean the assumption that the purely mechanical tendency of the free electron gas is toward equality of pressure throughout the metal. Under this hypothesis the condition of equilibrium in a detached metal bar having an established and permanent temperature gradient is expressed by the equation

$$k_f\left(\frac{1}{ne}\frac{dp}{dl} + \frac{dP}{dl} + \frac{dP_f}{dl}\right) = -k_a\left(\frac{dP}{dl} + \frac{dP_a}{dl}\right) \qquad (3)$$

This comes from equation (1) of my paper in these Proceedings for April, 1918, by substitution for μ according to equation (2) of that paper, which *should be*

$$\mu = k_f \frac{1}{Cne^2}$$

The first member of (3) as just given is the strength of the free electron current, down the temperature gradient, and the second member is the strength of the associated electron current, up the temperature gradient, per unit cross-section of the bar. We can rewrite (3) as follows, taking, for simplicity, the case in which $(dT \div dl) = 1$:

$$k_f\left(\frac{1}{ne}\frac{dp}{dT} + \frac{dP}{dT} + \frac{dP_f}{dT}\right) = -k_a\left(\frac{dP}{dT} + \frac{dP_a}{dT}\right) \qquad (4)$$

The term $(dP_f \div dT)$ expresses a possible differential attraction of the unequally heated metal for the free electrons, tending to move them down the temperature gradient, something distinct from the force due to the gradient of potential $(dP \div dT)$, which the gas pressure drift

of the free electrons produced. The term $(dP_g \div dT)$ has a corresponding meaning, with reference to the associated electrons.

The relation between E and T, being expressed by equation (2), we must suppose at least one of the ratios $(dP_f \div dT)$ and $(dP_g \div dT)$ to have a finite value. I shall assume the value of $(dP_g \div dT)$ to be negligible, and therefore we shall have, from equation (2),

$$\frac{dP_f}{dT} = \frac{K}{e}(s + 2.5), \tag{5}$$

Since

$$p = nKT, \tag{6}$$

and, according to a previous assumption,

$$n = zT^q, \tag{7}$$

where z and q are constants, we have

$$\frac{1}{n}\frac{dn}{dT} = K\left(1 + \frac{T}{dT}\frac{dn}{n}\right) = K(1 + q), \tag{8}$$

Substituting from (5) and (8) in (4) and taking $(dP_g \div dT)$ as zero, we get

$$\lambda\left(\frac{K}{e}(s + q + 1.5) + \frac{dP}{dT}\right) = -k_e\frac{dP}{dT} \tag{9}$$

According to my conception of thermal conduction, we have only to multiply either side of this equation by λ, the amount of energy required to free $(1 \div e)$ electrons within the metal, to get the value of θ, the thermal conductivity of the metal. That is, we can write

$$\theta = -\lambda k_e\frac{dP}{dT} \text{ ergs cm., sec., deg. C.} \tag{10}$$

We must now deal with the individual factors in the second member of this equation. From (9), remembering that $k = k_e + k_f$, we get

$$\frac{dP}{dT} = -\frac{Kk_f}{ek}(s + q + 1.5), \tag{11}$$

and λ is $(1 \div e)$ times the λ' of equation (1).

Hence we have

$$\theta = \frac{K^2}{e^2}\left(\frac{\lambda'_0}{k} + e\right)k_e\frac{k_f}{k}(s + q + 1.5). \tag{12}$$

Of course, since k is known, k_e is known if k_f is known. Substantially, my method of procedure with each metal is to find by trial values of λ_0', s, $(k_f \div k)$, and q, that will in combination account for Bridgman's value of σ, the Thomson effect, and then from the many combinations that will do this to find the smaller number that will account also for the known value of θ. Ultimately I must undertake to find from the combinations that meet these two tests the ones that will account for or be consistent with the Peltier effect, but I shall not do that in this paper.

In the following tables, as in the corresponding tables of the March paper, the metals are divided into four groups according to the values of K_1 and K_2 in the equation $\sigma = K_1 + K_2\theta$. Two alloys, also, constantan and manganin, are dealt with according to the data given for them by Bridgman. In finding k_{100}, the electrical conductivity at 100° C., from k_0, the conductivity at 0° C., I have used Bridgman's temperature coefficients, but he, working with very fine wires, did not determine the absolute conductivity at any temperature. The values of θ_0 and θ_{100} given in the first line beneath the name of any metal are derived from the work of Jaeger and Diesselhorst, except in those cases where a footnote is referred to. They are expressed in cal. cm. sec. deg. C. C, C_1 and C_2 are constants in the equation

$$(K_1 + K_2\theta) = C + C_1\theta + C_2\theta^2$$

The δ_0 of these tables is the constant part of the "ionizing potential" expressed in volts, δ_0' is the total ionizing potential at 0° K., and δ_{100}' is the total ionizing potential at 100° C.

The letter y indicates the estimated percentage of atoms which are ionized at 0° C. The method of estimation is given later.

First Group. Metals for which $K_1 = 0$ and $K_2 = 0$

TABLE 1. COBALT.

$k_0 = 102 \times 10^{-6}$; $k_{100} = 74.7 \times 10^{-6}$; $\theta_0 = 0.161$; $\theta_{100} = 0.164$; $\theta_0 + \theta_{100} = 0.325$

$\alpha = 7.8$ *I* ergs deg. C.

If $q = 1.55$ and $s = 4$ and $\lambda'_0 = 42$ *K*. $C_1 = 230 \times 10^{-6}$ and $s = 0.250$

$\left(\frac{kJ}{k}\right)_{100}$	y	δ_1	δ_2	δ_{100}	$\left(\frac{dV}{dt}\right)_0$	$\left(\frac{dV}{dt}\right)_{100}$	$\frac{\delta_{0'}}{\alpha \cdot 100}$	$\frac{\delta_{100'}}{\alpha \cdot 100}$	θ_0	θ_{100}	$\frac{\delta_1}{\delta_{100}}$
0.279	6.7%[1]	0.084	0.088	0.132	−8020	−9720	76.0	54.0	0.152	0.165	0.95

[1] Lacking observed values of θ_0 and θ_{100} for cobalt, I have estimated the values here given by use of the Wiedemann-Franz ratio (average for 13 metals) applied to k_0 and k_{100}.

TABLE 2. NICKEL.

$k_0 = 93 \times 10^{-6}$; $k_{100} = 62.5 \times 10^{-6}$; $\theta_0 = 0.143$; $\theta_{100} = 0.138$; $\theta_0 + \theta_{100} = 1.01$

$\alpha = 3.36$ *I* ergs deg. C.

If $q = 1.55$ and $s = 4$ and $\lambda'_0 = 100$ *K*. $C_1 = 105 \times 10^{-6}$ and $s = 0.250$

0.250	5.7%	0.080	0.103	0.137	−8130	−8710	70.8	46.9	0.144	0.133	1.08

TABLE 3. PALLADIUM.

$k_0 = 100 \times 10^{-6}$; $k_{100} = 75.0 \times 10^{-6}$; $\theta_0 = 0.105$; $\theta_{100} = 0.102$; $\theta_0 + \theta_{100} = 0.91$

$\alpha = 3.52$ *I* ergs deg. C.

If $q = 1.0$ and $s = 6$ and $\lambda'_0 = 114$ *K*. $C_1 = 90.8 \times 10^{-6}$ and $s = 0.1087$

0.106	3.2%	0.010	0.151	0.203	−5180	−5550	98.1	67.9	0.108	0.182	0.92

$\sigma = 0.0662$ *I* ergs deg. C

$H_{20} = 3.4$ mm. $\lambda = 0.0$ mm. $\lambda' = 117$ *K*, $C_1 = 15.2 \times 10^{-8}$ and $C' = 0.0652$

0.0620	2.37	0.0	0.0158	0.0245	5980	4760	103	74	0.170	0.175	0.97

TABLE 5. TIN

$k_1 = 165 \times 10^{-6}$, $k_m = 57.6 \times 10^{-6}$, $\theta_o = 0.137$, $\theta_{100} = 0.145$; $(\theta_o + \theta_{100}) = 1.08$

$\sigma = 0.134$ *I* ergs deg. C

$H_{20} = 3.52$ mm. $\lambda = 0$ mm. $\lambda' = 234$ *K*, $C_1 = 1.97 \times 10^{-8}$ and $C' = 0.0166$

0.0447	2.37	0.0	0.0798	0.212	3210	3220	100	69.2	0.150	0.147	1.08

TABLE 6. ZINC

$k_1 = 180 \times 10^{-6}$, $k_m = 3.5 \times 10^{-6}$, $\theta_o = 0.260$ $\theta_{100} = 0.262$, $(\theta_o + \theta_{100}) = 1.02$

$\sigma = 0.301$ *I* ergs deg. C

$H_{20} = 3.55$ mm. $\lambda = 10$ mm. $\lambda' = 117$ *K*, $C_1 = 11.61 \times 10^{-8}$ and $C' = 0.0304$

0.0954	1.67	0.0	0.245	0.313	2630	2780	175	123	0.268	0.265	1.01

Metals for which $K_1 < 0$ and $K_2 = 0$.

TABLE 7. BISMUTH

$k_1 = 9.3 \times 10^{-6}$, $k_m = 600 \times 10^{-6}$, $\theta_o = 0.0230$, $\theta_{100} = 0.0161$; $(\theta_o + \theta_{100}) = 1.25$

$\sigma = -3.2$ *I* ergs deg. C

$H_{20} = 1.25$ mm. $\lambda = 78$ mm. and $\lambda' = 1150$ *K*, $C_1 = -1226 \times 10^{-8}$ and $C' = 0.540$

0.528	2.37	0.148	0.166	0.280	−11800	−11000	4.28	3.05	0.0230	0.0160	1.25

CADMIUM

$k_1 = 160 \times 10^{-6}$, $k_m = 13.4 \times 10^{-6}$, $\theta_o = 0.225$, $\theta_{100} = 0.216$, $(\theta_o + \theta_{100}) = 1.03$

$\sigma = -32.4$ *I* ergs deg. C

It is easy to find values of q_1 and λ'_2 that will give the right value for θ_o, but the value of θ_{100} that results is much too small. I cannot deal satisfactorily with cadmium at present, owing to the very large negative value that Bridgman finds for its σ, a value which is about ten times as great as those deducible from the work of various other investigators who have studied the thermoelectric behavior of this metal. See, for example, a paper by Dewar and Fleming, *Phil. Mag.*, Vol. 40, 5th Series, 1895. It is possible that Bridgman has made some mistake in this case.

TABLE 8 — COBALT

$k_a = 650 \times 10^{-6}$, $k_{cm} = 45 \times 10^{-6}$, $\theta_a = 0.653$, $\theta_{cm} = 0.703$, $\theta_a - \theta_{cm} = 1.01$

$\sigma = -0.004\ 2$ ergs/deg. K

If $q = 1.49$ and $s = 9$ and $\lambda'_a = 1.24\ K$, $C_1 = 12.4 \times 10^{-6}$, $C_2 = 1.15 \times 10^{-6}$, $C = 0.0132$

$\left(\frac{k'}{k}\right)_{cm}$	s	k_a	λ_a	λ_{cm}	$\left(\frac{\sigma T}{\rho}\right)_a$	$\left(\frac{\sigma T}{\rho}\right)_{cm}$	$\frac{k_a}{k_{cm}}$	$\frac{\theta_a}{\theta_{cm}}$	λ_a	λ_{cm}	$\frac{\lambda_a}{\lambda_{cm}}$
0.030	6.4%	0.063	0.214	0.292	.2880	.2780	0.26	1.29	0.918	0.852	1.08

TABLE 9 — MAGNESIUM

$k_a = 240 \times 10^{-6}$, $k_{cm} =$?, mean θ between 0° and 100° $= 0.154$

$\sigma = -0.008\ 1$ ergs/deg. K

If $q = 1.490$ and $s = 6.5$ and $\lambda'_a = 800\ K$, $C_1 = 11.4 \times 10^{-6}$ and $C = 0.0082$

0.060	12%[1]	0.039	0.192	0.248	−3700	−3200	221	1	0.370	1	1

TABLE 10 — SILVER

$k_a = 670 \times 10^{-6}$, $k_{cm} = 126 \times 10^{-6}$, $\theta_a = 1.01$, $\theta_{cm} = 0.99$, $\theta_a - \theta_{cm} = 1.02$

$\sigma = -0.004\ 1$ ergs/deg. C

If $q = 1.49$ and $s = 11.5$ and $\lambda'_a = 30\ K$, $C_1 = -8.8 \times 10^{-6}$ and $C = 0.0240$

0.023	5.5%[1]	0.063	0.272	0.370	−2580	−2280	655	400	1.01	0.94	1.08

TABLE 11 — TUNGSTEN

$k_a = 140 \times 10^{-6}$, $k_{cm} = 101 \times 10^{-6}$, $\theta_a = 0.15$, $\theta_{cm} =$?

$\sigma = -3.41\ T$ ergs/deg. K

If $q = 1.49$ and $s = 9$ and $\lambda'_a = 184\ K$, $C_1 = -41.4 \times 10^{-6}$ and $C = 0.0026$

0.005	3.2%[1]	0.002	0.213	0.280	−5380	−5630	130	89	0.455	0.344	1.03

[1] Value found by Coolidge

Third Group. Metals for which $K_1 > 0$ and $K_2 > 0$.

TABLE 12 — IRON

$k_a = 78 \times 10^{-6}$; $k_{cm} = 48 \times 10^{-6}$, $\theta_a = 0.163$, $\theta_{cm} = 0.151$, $\theta_a - \theta_{cm} = 1.08$

$\sigma = (0.78\ T + 0.04\ H^2)$ ergs/deg. C

If $q = 1.205$ and $s = 11$ and $\lambda'_a = 117\ K$, $C'_1 = 26.9 \times 10^{-6}$, $C_2 = 14.8 \times 10^{-6}$, $C = 0.0264$

0.041	1.2%	0.01	0.268	0.363	−3350	−3740	75.2	40.2	0.161	0.149	1.08

TABLE 13 — THALLIUM

$k_a = 57 \times 10^{-6}$; $k_{cm} = 43.9 \times 10^{-6}$, $\theta_a = 0.080\ 0$, $\theta_{cm} = 0.080\ 5$, $\theta_a - \theta_{cm} = 0.994$

$\sigma = (0.208\ T \times 0.000\ 330\ H^2)$ ergs/deg. C

If $q = 1.48$ and $s = 7$ and $\lambda'_a = 117\ K$, $C'_1 = 2.80 \times 10^{-6}$, $C_2 = 1.56 \times 12^{-6}$, $C = 0.0020$

0.068	1.9%	0.01	0.174	0.230	−4000	−4100	58.1	41.0	0.089	0.084	0.95

[1] See footnote under table 1, cobalt

TABLE 14 ALUMINIUM

Isotropic metal *Metals for which* $K_1 = 0$ *and* $K_2 > 0$

$k_e = 4.80 + 2.04 \times 10^{-4} T$, $k_{ph} = 7.00 + 10^{-4} T$, $\theta_e = 0.417$; $\theta_{ph} = 0.492$; $(\theta_e + \theta_{100}) = 0.97^1$
$\sigma = 0.0366\, T + 0.0386\, T^2$ ergs/deg. C.
$H_q = 1.45$ and $z = 8$ and $\lambda'_0 = 125\, K$, $C_1 = 0.35 \times 10^{-4}$, $C_1 = -3.04 \times 10^{-4}$, $C = 0.0886$

$\left(\frac{k_{ph}}{k}\right)_{18^\circ}$	γ	α_1	α_2	α_{273}	$\left(\frac{dT}{dt}\right)_e$	$\left(\frac{dT}{dt}\right)_{ph}$	$(k_a)_0 \times 10^6$	$(k_a)_{100} \times 10^6$	θ_0	θ_{100}	$\frac{\theta_0}{\theta_{100}}$
0.089	11°	0.0215	0.110	0.182	4120	−4170	346	241	0.479	0.449	1.07

[1] Lees found $\theta_0 = 0.524$ in this metal, but apparently he did not determine θ_{100}

TABLE 15 GOLD

$k_e = 4.80 + 10^{-4} k_{ph} = 3.51 + 10^{-4} \theta_e = 0.699$; $\theta_{100} = 0.703$; $(\theta_0 + \theta_{100}) = 0.994$
$\sigma = (-0.931\, T + 0.001\, T^2)$
$H_q = 1.495$ and $z = 8$ and $\lambda'_0 = 15\, K$, $C_1 = 0.73 \times 10^{-4}$, $C_1 = -13.7 \times 10^{-8}$, $C = 0.0486$

0.047	8°,	0.0062	0.100	0.250	3340	−3290	466	335	0.705	0.672	1.05

TABLE 16 MOLYBDENUM

$k_e = 2.74 + 10^{-4} k_{ph} = 1.91 + 10^{-4} \theta_e = 0.43(?)$,[1] $\theta_{100} = 0.42(?)$,[1] $(\theta_0 + \theta_{100}) = 1.02(?)$
$\sigma = (-4.33\, T + 0.015\, T^2)$ ergs/deg. C.
$H_q = 1.5$ and $z = 10$ and $\lambda'_0 = 110\, K$, $C_1 = 8.7 \times 10^{-4}$, $C_1 = -51 \times 10^{-8}$, $C = 0.0338$

0.0296	2.8°,	0.0001	0.244	0.330	2850	−2490	265	185	0.439	0.363	1.21

[1] See footnote under table 1, cobalt

ALLOYS

TABLE 17 CONSTANTAN

$k_e = 20.4 + 10^{-4} k_{ph} = 20.4 \times 10^{-4} \theta_e = 0.052$, $\theta_{100} = 0.004$, $(\theta_0 + \theta_{100}) = 0.81$
$\sigma = 7.94\, T$ ergs/deg. C.
$H_q = 1.53$ and $z = 5$ and $\lambda'_0 = 90\, K$, $C_1 = 188 \times 10^{-8}$ and $C = 0.288$

0.300[1]	1°,	0.008	0.120	0.160	12500	−13300	14.5	14.2	0.054	0.076	0.71

[1] Very roughly estimated from the values of γ given for copper and nickel.

TABLE 18 MANGANIN

$k_e = 2.18 + 10^{-4} k_{ph} = 2.38 \times 10^{-4} \theta_e = 0.051$, $\theta_{100} = 0.003$; $(\theta_0 + \theta_{100}) = 0.81$
$\sigma = (-0.828\, T - 0.00072\, T^2)$ ergs/deg. C.
$H_q = 1.51$ and $z = 4.5$ and $\lambda'_0 = 90\, K$, $C_1 = -8.74 \times 10^{-8}$, $C_1 = -18.0 \times 10^{-8}$
$C = 0.27$

0.267	1°,	0.0008	0.115	0.152	10500	−10400	17.4	17.5	0.049	0.066	0.75

[1] See footnote under table 17

Conclusion. There is a constant relation in the value of $\theta_{\infty} : \theta_{273}$ for any metal, as found by the method of this paper. There is one case except that of Co, where a great range of $\theta_{\infty} : \theta_{273}$ was found, and the value of $\theta_{\infty} : \theta_{273}$ change from < 1 to > 1 with any variation of χ_0 and λ'_0. Out of seventeen cases, including those of constantan and manganin, the value of $\theta_{\infty} : \theta_{273}$, as found by experiment or calculated by the use of the Wiedemann Franz ratio, is in nine greater than 1 and in eight less than 1. In only two of these cases, those of aluminium and gold, does the method of this paper fail to give a value of $\theta_{\infty} : \theta_{273}$ on the right side of 1.

In nine of these seventeen cases, Bi, Co, Fe, Ni, Pd, Pt, Sn, Tl, Zn, it has been found practicable to get a combination of χ_0 and λ'_0 that will account for Bridgman's σ and give the desired values of both θ_0 and θ_{∞} to any reasonable degree of accuracy. In all of these nine cases, except that of Bi, the value of K_0 in the equation $\sigma = K_0 T + K_2 T^2$ is positive.

In six of the other eight cases the value of $\theta_{\infty} : \theta_{273}$ here found is larger than the one found by experiment or indicated by the 1 : 2 rule. In four cases, Ag, Al, Au, Cu, the discrepancy is about 6 to 10%; in one, that of Mo, it may be considerably greater, but this is a 1 : 2 case, in only one, that of Cd, is the disagreement hopelessly great. In constantan and in manganin the calculated $(\theta_0 : \theta_{273})$ is less than the observed.

The value of γ, the percentage of ionized atoms within a metal, has been estimated by means of the formula[1]

$$k_t = \frac{n e^2 l}{4 R T}$$

When T is taken as 273, we have, approximately,

$$k_t = 1.91 \times 10^{-22} n l = 1.91 \times 10^{-22} \gamma \nu l,$$

or

$$\gamma = 5.24 \times 10^{22} (k_t \div \nu l),$$

where ν is the number of atoms of the metal per cu. cm. and l is the length of the "mean free path" of the electrons among the atoms.

Concerning the value of l, I have been and am still much in doubt. Adams and Chapman, in a study of the Corbino effect,[2] estimated it to be in copper not far from 3×10^{-7} cm., which is about 13 times the distance from centre to centre of adjacent atoms, if a cubical arrangement of the atoms is assumed. Compton, K. T., and Ross[3] concluded that a photo-electrically excited electron may move about 2.67×10^{-7} cm. in platinum, about 11 times the centre to centre distance of the atoms, and approximately 5×10^{-7} cm. in gold, nearly 20 times the atomic distance. I have taken l as 10 times the atomic distance, thus putting $l = (10 \div \nu^{\frac{1}{3}})$ and making

$$\gamma = 0.52 \times 10^{23} \times k_t \div \nu^{\frac{4}{3}}.$$

A much smaller estimate of l than the one I have used would be disastrous for my speculations, as it would give large values of γ and thus in-

produce an inexplicable difficulty regarding specific heat. Even with the assumption that I have made as to the length of l, the influence of the free electrons, and still more the influence of ionization with increase of temperature, on the specific heat, presents a rather serious question. Thus, to take what is probably the most unfavorable case set forth in the preceding table, that in Mg, $q = 1.5$ and $s = 6.5$ and $\lambda'_0 = 460\ R$ and $\gamma = 12^\circ$, we have as the heat absorbed by the free electrons in the rise of 1 gm of Mg from 0° C. to 1° C., 0.025 cal., while the heat required by the accompanying ionization is 0.124 cal., a total of 0.149 cal., which is rather more than half the total specific heat of Mg at 0° C. It would be easy, however, to choose values of q, s and λ'_0 for Mg which would serve the purpose of this paper while affecting the specific heat less. Moreover, it is possible that l may be greater than I have taken it to be.

Table IV of my paper in these *Proceedings* for March, 1920, now requires revision. Al, Fe, Mo and Tl going into Section (A); but the general testimony of the table remains unchanged, the *mean* of the last column being now -1.40°, for Section (A) and $+2.47^\circ$, for Section (B).

It remains to be seen whether the theory I am developing can deal successfully with the Peltier effect. A preliminary examination, already made, of this matter is encouraging.

[1] Equipartition of energy, as holding for electrons *within* an atom, cannot be regarded as an established principle.

[2] *Phys. Rev.*, *Lincoln*, April 1918, 129.

[3] In my previous paper λ had a different meaning.

[4] *London Phil. Mag.* **28**, 1914, 692, 702.

[5] *Phys. Rev.*, *Lincoln*, May 1919, 374, 391.

THE BOHR THEORY AND THE APPROXIMATE HARMONICS IN THE INFRA RED SPECTRA OF DIATOMIC GASES.

By Edwin C. Kemble.

Abstract.

Infra-red spectra of diatomic gases, a quantum theory. The author's earlier theoretical explanation of the occurrence of *approximate harmonics* in the infra-red spectra of HCl, HBr and HI, based on the non linearity of the law of force governing the relative displacement of the component atoms, encountered three difficulties: it did not explain the inexactness of the harmonics, it gave a wrong ratio for the asymmetry constants of the fundamental and harmonic bands, and it was in serious conflict with Rubens' data. It is now shown that by *adopting Bohr's hypotheses* that the molecules possess a series of discrete, non-radiating states of vibration and that the frequency of radiation and absorption are determined by the energy emitted or absorbed, a new explanation is obtained which seems to overcome the difficulties mentioned above. In connection with the discussion the author presents a full account of his theory of the appearance of the bands which postulates a decrease in the frequency of vibration of a rotating diatomic molecule with increasing angular velocity, a consequence of the non linearity of the law of force. It is found that the theory gives the observed value of the ratio of the asymmetry constants only if it is assumed that the minimum kinetic energy for vibratory motion is not finite as for rotary motion in the Bohr theory, but is zero.

Rubens' law suggests irradiation. The author's theory of the structure of these band spectra is based on a theory which involves a minor contradiction to Kirchhoff's law. This leads to the conclusion that the ratio of the intensities of any two corresponding parts of an absorption band is independent of the temperature. This suggests that Kirchhoff's law may not hold in such cases.

Introduction.

In 1910 the writer published a theoretical paper[1] predicting the occurrence of weak harmonics to the principal absorption bands in the infra-red spectra of diatomic gases. The theory was based on the assumption that the form of the electromagnetic waves radiated or absorbed by an oscillating dipole must be related to the form of the vibration in the manner indicated by the classical electromagnetic theory. It was shown that, on account of the non-linearity of the law of force governing the relative displacement of the atoms of a diatomic molecule, vibrations of these atoms along their line of centers having the amplitudes called for by the quantum theory must depart considerably from the simple harmonic type. According to Fourier's theorem the

[1] Phys. Rev. Dec. 1916, p. 393.

of emitted frequencies must also be absorbed. The infra-red absorption bands of diatomic gases, which are believed to have their origin in the atomic vibrations under consideration, should accordingly be accompanied by faint harmonics. As an example of the occurrence of such faint harmonics, the infra-red absorption bands of carbon monoxide were cited at the time, while a later paper[1] by Dr. J. B. Brinsmade and the writer reported the discovery of similar harmonic absorption bands in the infra-red spectra of HCl and HBr, which were held to constitute a verification of the theory.

There were, however, three difficulties in connection with the above explanation of the observations, *viz.*, (*a*) the fact that the observed harmonics seemed not to be exact, the wave length of the center in each case being from 0.025 μ to 0.045 μ greater than its calculated value, (*b*) the fact that the relation between the asymmetry constants of the fundamental and harmonic absorption bands in the HCl spectrum was not that predicted by the theory, and (*c*) the incompatibility of the theory itself with Kirchhoff's law. In the absence of an alternative explanation of the phenomena, and in view of the inherent plausibility of the explanation given above, the writer was inclined to attribute the discrepancies (*a*) and (*b*) to a slight error of unknown origin in the dispersion curve for quartz used in calculating the wave lengths, and to assume that these harmonics constitute a *bona fide* exception to Kirchhoff's law. He now desires to report that the hypotheses adopted by Bohr in his theory of radiation and of atomic structure afford an alternative explanation of the observed phenomena which seems to avoid the above-mentioned difficulties.

The Application of Bohr's Hypotheses to Radiation from Vibrating Diatomic Molecules.

We proceed to the application of Bohr's hypotheses to the radiation from a vibrating diatomic molecule. The molecules are assumed to possess a series of discrete, non-radiating, steady, possible states of vibration. Let τ denote the number of any of these steady states, and let W_τ denote the corresponding energy of vibration. The law of force governing the motion being nonlinear, the frequency of vibration, ω, will depend upon the energy and therefore upon τ. In accordance with the earlier form of Planck's theory we assume that the energy of vibration is always an integral multiple of $h\omega$. (See supplementary note). Thus

$$W_\tau = \tau h\omega, \qquad \tau = (0), 1, 2, 3, \cdots. \quad (1)$$

[1] J. B. Brinsmade and E. C. Kemble, Proc. Nat. Acad. Sci., 3, 1917 (420).

According to the Bohr theory the angular momentum of an electron attached to a single hydrogen atom cannot be reduced below the minimum value $h/2\pi$. The observed structure of the infra-red absorption bands of HCl indicates that the above remark is also true of the angular momentum of a diatomic molecule.[1] These considerations create the presumption that the energy of any vibratory degree of freedom as well as that of any rotational degree of freedom must always be greater than zero, in accordance with which zero should be eliminated from the list of the possible values of τ in the above equation. There is some evidence in the present theory, however, that such a generalization is incorrect, and the question will accordingly be left open.

With Bohr we add the hypothesis that the frequency of the radiation emitted or absorbed by the molecule in passing from the steady state τ_1 to the steady state τ_2 is given by the relation

$$\nu = \frac{1}{h}(W'_{\tau_1} - W'_{\tau_2}). \tag{2}$$

Combining these assumptions, we obtain the following expression for the radiation frequencies emitted or absorbed:

$$\nu = \frac{1}{h}(\tau_2\omega_2 - \tau_1\omega_1). \tag{3}$$

If the frequency of vibration were completely independent of the amplitude, as in the case of an ideal linear oscillator, the frequencies emitted and absorbed would all be integral multiples of ω. If the frequency of vibration is nearly independent of the amplitude, the frequencies of the radiation emitted and absorbed will be approximately integral multiples of the frequency of vibration for small amplitudes. This theory, therefore, like the other, predicts the occurrence of (approximate) harmonics, though it gives them a different interpretation. The fundamental absorption band is due to the molecules jumping from the first of the steady states of vibration to the second (at ordinary temperatures the number of molecules normally in the second steady state is infinitesimal), while the first harmonic is due to the molecules jumping from the first steady state to the third.

Let us now see how the present theory meets the difficulties encountered by the former

Wave-lengths of "Harmonics."

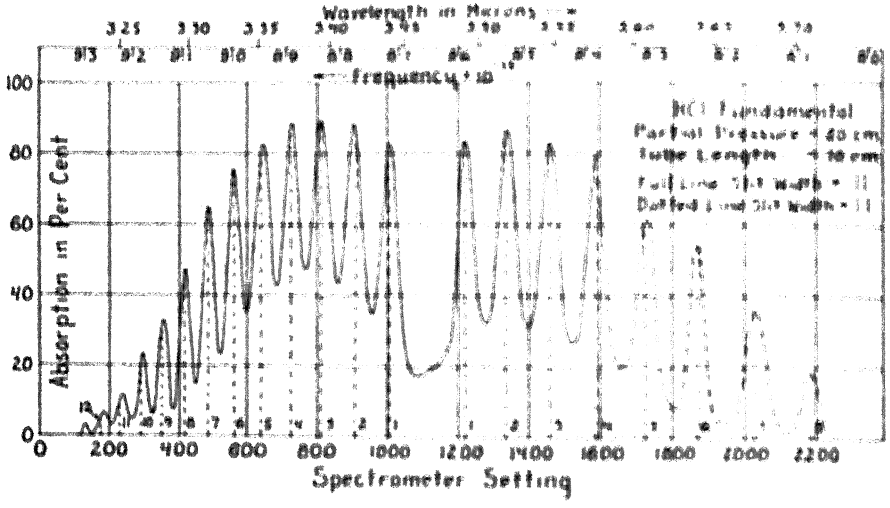
The fact that the wave-length of the center of the "harmonic" band is in each case observed to be a little more than half of the wave-length of the fundamental fits perfectly with the new theory. We may assume as a first approximation for small amplitudes that the equation

[1] Bjerrum and Kemble, *l. c.*, p. 421

$$m\frac{d^2x}{dt^2} = -k_2x - k_3x^2. \qquad (4)$$

In this case, whatever the sign of k_3, the frequency of vibration decreases when the amplitude increases.[1] Consequently the energy of a molecule should increase by a smaller amount when the molecule passes from the second steady state to the third than when it passes from the first to the second, and the frequency absorbed in passing from the first steady state to the third should be a little less than twice that absorbed in passing from the first to the second.

In order to show that the present theory is in qualitative agreement with the observed relative asymmetry of the two infra-red absorption



bands of HCl it is necessary to indulge in some mathematical analysis. The writer has never published a full account of his theory of the asymmetry of the infra-red absorption bands of diatomic gases[2] and therefore welcomes this opportunity to present that theory in complete form.

The Asymmetry of the Infra-red Absorption Bands of Diatomic Gases.

According to the elementary theory of the structure of the infra-red absorption bands of diatomic gases given by Bjerrum[3] each of these

[1] Reference No. 1, p. 708.

[2] The theory was first stated in an unpublished paper bearing the title "The Infra-red Absorption Bands of Gases and the Application of the Quantum Theory to Molecular Rotations" read before the American Physical Society on December 28, 1916. A brief statement of the essentials of the theory is to be found in the paper by Bäumler and Kemble cited above.

[3] N. Bjerrum, Nernst Festschrift, Halle, 1912, Verh. d. D. Physik. Ges., 16, 1914 (640).

bands owes its width primarily to the effect of the molecular rotations and should be composed of a double series of elementary bands or quantum lines. These elementary bands are themselves of quite appreciable breadth, but in order to distinguish them from the composite band which they unite to form, it will be convenient to designate them in the remainder of this paper as "quantum lines." The molecules are assumed to vibrate with a common frequency ω. The radiation emitted and absorbed by the molecules which rotate with the frequency ν_r is divided between the frequencies $\omega + \nu_r$ and $\omega - \nu_r$. Consequently the molecules having any given angular velocity give rise to a pair of narrow absorption lines whose separation on the frequency scale is twice the frequency of the rotation. According to the quantum theory the frequencies of rotation must all be integral multiples of a certain basic frequency which we denote by the symbol ν_1. Hence the only frequencies radiated or absorbed are those given by the formula

$$\nu = \omega \pm p\nu_1, \qquad p = 1, 2, 3, \cdots. \quad (5)$$

Thus the quantum lines corresponding to different values of p should be equally spaced. Since the two absorption lines corresponding to each value of p are due to the same group of molecules, they should be of nearly equal intensity, while the intensities of the lines corresponding to different values of p should vary with the numbers of molecules in the corresponding groups. Consequently the large band of which these lines are the components should have the general appearance of a symmetrical doublet.

The accompanying figure shows the appearance of the principal band in the infra-red spectrum of HCl as observed by Dr. Brinsmade and the writer.[1] Instead of being equally spaced, the quantum lines are obviously closer together on the high frequency side and it is evident that if the band is observed with a spectrometer of low resolving power it will appear to be an asymmetric doublet, the high frequency maximum being the more intense. This group of lines and the approximately harmonic group in the same spectrum are the only infra-red absorption bands in the spectra of the diatomic gases which have been resolved into their elementary components, but the infra-red absorption bands of the other diatomic gases are similarly asymmetric doublets.

In the writer's opinion the asymmetry is due to a decrease in the frequency of vibration with increasing angular velocity. This decrease results from the nonlinearity of the law of force which governs the vibratory motion.

In order to reduce the above hypothesis to quantitative form, we

molecule. It will be assumed that the masses of the two atoms, m_1 and m_2, are concentrated in the nuclei. Let ζ denote the distance between the atomic centers and let

$$m = m_1 m_2 / (m_1 + m_2).$$

Let θ denote the angle between the line of the atomic centers and any fixed line in the plane of the motion. With this notation the expression for the kinetic energy of the system is readily reduced to the form

$$T = \frac{m}{2}\left[\left(\frac{d\zeta}{dt}\right)^2 + \zeta^2\left(\frac{d\theta}{dt}\right)^2\right]. \tag{6}$$

Denoting the potential energy by $\Phi(\zeta)$ and setting up Lagrange's equations, we have

$$\frac{d}{dt}(m\dot{\zeta}) - m\zeta\dot{\theta}^2 + \Phi'(\zeta) = 0 \tag{7}$$

and

$$\frac{d}{dt}(m\zeta^2\dot{\theta}) = 0. \tag{8}$$

Equation (8) gives rise to the statement of the constancy of the angular momentum. This may be written

$$m\zeta^2\dot{\theta} = m\zeta_0^2\Omega_0, \tag{9}$$

where ζ_0 is assumed to be the distance between the nuclei when the molecule is in equilibrium and at rest, while Ω_0 is the angular velocity of the moving molecule when ζ passes through the value ζ_0. Substituting from (9) into (7) we obtain the differential equation for the vibratory motion:

$$m\frac{d^2\zeta}{dt^2} = -\Phi'(\zeta) + m\frac{\Omega_0^2\zeta_0^4}{\zeta^3}. \tag{10}$$

Let U denote the total energy of vibratory and rotational motion, and let ζ_1 and ζ_2 denote the minimum and maximum values of ζ. Integration of equation (10) then gives the following expression for the period of the vibration:

$$\tau = \sqrt{2m}\int_{\zeta_1}^{\zeta_2} \frac{d\zeta}{\sqrt{U - \Phi(\zeta) - \frac{m\Omega_0^2\zeta_0^4}{2\zeta^2}}}. \tag{11}$$

Obviously ζ_1 and ζ_2 are roots of the equation

$$U - \Phi(\zeta) - \frac{m\Omega_0^2\zeta_0^4}{2\zeta^2} = 0. \tag{12}$$

Ω_0 can be identified with the mean angular velocity of the molecule

without appreciable error and equation (11) shows that the period of vibration is a function of Ω_0. It also shows that if τ, or its reciprocal, the frequency of vibration, ω, is expanded into a power series in Ω_0, the coefficients of the odd powers must vanish, since a reversal of the sign of Ω_0 cannot affect the value of ω. Denoting the frequency of rotation by ν_r, and the frequency of vibration for zero angular velocity by ω_0, we may therefore write as a first approximation

$$\omega = \omega_0 - a\beta^2\nu_r^2. \tag{13}$$

The coefficient a is a function of the total vibrational energy W. It will be shown later on that in general we may expect a to be positive.

If we adopt the fundamental hypothesis of the writer's earlier work, which identifies the frequency of vibration of the molecule with the mean of the two radiation frequencies absorbed (or radiated), and combine equations (5) and (13), we obtain

$$\nu = \omega_0 - a\beta^2\nu_r^2 \pm p\nu_r. \tag{14}$$

This is the equation for the position of the quantum lines given in the writer's former brief statement of the theory of asymmetry.[1] If the values of ω_0, a, and ν_r are properly chosen, the formula gives the frequencies of the quantum lines in the HCl fundamental with considerable accuracy (cf. the vertical dashed lines in the figure[2]).

The positions of the lines in a true harmonic should be given by

$$\nu = 2\omega_0 - a\beta^2\nu_r^2 \pm p\nu_r. \tag{14a}$$

Equation (14a) is of the same form as (14) and gives the frequencies of the quantum lines in the observed harmonic correctly if the values of the constants ω_0 and a are readjusted. No readjustment of the value of ν_r is necessary.

Equation (5), however, does not fit with the fundamental hypotheses regarding the nature of the process of radiation on which the present paper is based. In order to bring the theory of asymmetry into line with the Bohr theory we must assume that equation (3) gives the mean of the two frequencies emitted and absorbed by any one group of molecules.[3] Confining our attention to the process of absorption, we replace equation (5) by

$$\nu = \tau_1\omega_{\tau_1} - \tau_2\omega_{\tau_2} \pm p\nu_r \qquad \begin{cases} p = 1, 2, 3, \cdots, \\ \tau_2 > \tau_1. \end{cases} \tag{15}$$

[1] Brinsmade and Kemble, l. c., p. 424.

[2] The consistent discrepancy in the outermost quantum lines on the high frequency side is completely eliminated without the introduction of fresh arbitrary constants if the change in the moment of inertia due to the expansion of the molecule with increasing angular velocity is taken into account.

[3] An equivalent assumption has been used by Bohr to explain the Zeeman effect. Cf. Phil. Mag., 26, 1914 (1913).

on the energy of vibration, ω is to be regarded as a function of τ and p. Moreover, the constant a is a function of τ. We therefore introduce the notation

$$\omega = \omega + f^1$$

$$a = a + \dots$$

Equation (13) becomes

$$\omega(\tau, p) = \omega(\tau, 0) + \dots + f^1 \dots \tag{16}$$

Combining (15) and (16), we obtain

$$\begin{aligned} \nu &= \tau_2[\omega(\tau_2, 0) + a(\tau_2) p^2 v_2^2] \\ &= \tau_1[\omega(\tau_1, 0) + a(\tau_1) p^2 v_1^2] + f v_1 \end{aligned} \tag{17}$$

Let $N(\tau_1, \tau_2)$ and $\mathfrak{N}(\tau_1, \tau_2)$ be defined by the equations

$$\begin{aligned} N(\tau_1, \tau_2) &= \tau_2 \omega(\tau_2, 0) - \tau_1 \omega(\tau_1, 0), \\ \mathfrak{N}(\tau_1, \tau_2) &= \tau_2 a(\tau_2) - \tau_1 a(\tau_1) \end{aligned} \tag{18}$$

Then (17) becomes

$$\nu = N(\tau_1, \tau_2) + \mathfrak{N}(\tau_1, \tau_2) p^2 v_1^2 + f v_1 \tag{19}$$

This equation is of the same form as (14) and consequently gives the positions of the lines in either of the HCl bands with equal accuracy.

The specific expressions for N and $\mathfrak{N}$ for the fundamental and first harmonic differ according as we assume that zero is or is not a possible value of τ. If it is not, $\tau_1 = 1$ and $\tau_2 = 2$ for the fundamental. Thus

$$\begin{aligned} N &= 2\omega(2, 0) - \omega(1, 0), \\ \mathfrak{N} &= 2a(2) - a(1). \end{aligned} \tag{20}$$

In the case of the first harmonic we should then have $\tau_1 = 1$ and $\tau_2 = 3$. Denoting the values of N and $\mathfrak{N}$ for the first harmonic by the symbols N' and $\mathfrak{N}'$, we obtain

$$\begin{aligned} N' &= 3\omega(3, 0) - \omega(1, 0), \\ \mathfrak{N}' &= 3a(3) - a(1). \end{aligned} \tag{21}$$

If, on the other hand, we adopt the alternative hypothesis that zero is a possible value of τ, the above equations become

$$\begin{aligned} N &= \omega(1, 0); \\ N' &= 2\omega(2, 0); \\ \mathfrak{N} &= a(1); \\ \mathfrak{N}' &= 2a(2). \end{aligned} \tag{22}$$

In either case, if a were independent of the energy of vibration, $\mathfrak{N}'$

would be equal to $2\mathfrak{A}$. This relation is the same as that called for by the old theory and does not agree with experiment, since the observed value of the ratio of the asymmetry constants $\mathfrak{A}'$ and $\mathfrak{A}$ is a little less than 1.5. On the other hand, it decreases regularly as the energy of vibration increases, so it is to be expected in either case that the ratio of $\mathfrak{A}'$ to $\mathfrak{A}$ will be less than 2.

In order to justify fully the present revised theory of the structure of these infra-red absorption bands, it would be necessary to derive the observed values of the constants N, N', $\mathfrak{A}$, and $\mathfrak{A}'$ on the basis of a plausible form for the potential energy function Φ. Mathematical difficulties, however, stand in the way of such a complete solution of the problem, and for the present we must content ourselves with showing that the observed values of the constants mentioned are not unreasonable. To that end we shall assume a simple form for the potential energy function and shall study the variation in the frequency of vibration with the angular velocity and with the vibrational energy on the basis of the restricting hypothesis that the amplitude of the vibrations is small.

All that we can reasonably feel sure of in regard to the law of force which governs the motion of the atoms is that it is asymmetric in that the potential energy increases more rapidly when the atoms are compressed together than when they are drawn apart. A simple formula having the asymmetry suggested is obtained if the force is assumed to be composed of a constant attraction combined with a repulsion varying inversely as the nth power of the distance between the nuclei. The net repulsive force between the atomic centers will then be given by an expression of the form

$$\Phi'(\zeta) = a\zeta^{-n} - \beta, \tag{23}$$

where a and β are constants.

Since the force reduces to zero when ζ equals ζ_0,

$$\beta = a\,\zeta_0^{-n}.$$

Equation (10) becomes

$$m\frac{d^2\zeta}{dt^2} = a\left(\frac{1}{\zeta^n} - \frac{1}{\zeta_0^n}\right) + \frac{m\Omega_0^2\zeta_0^4}{\zeta^3}. \tag{24}$$

In order to integrate (24) we will throw it into the form (4) by means of approximations. Consider first the case where the angular velocity is zero. In this case it is convenient to expand $1/\zeta^n$ and $1/\zeta^3$ into power series about the point $\zeta = \zeta_0$. Let

$$\xi = \zeta - \zeta_0.$$

$$k = an\,\zeta_0^{n-2}, \tag{26a}$$

$$k_1 = -an(n-1)\,\zeta_0^{n-2}. \tag{26b}$$

According to Seeliger[1] the following equations constitute an approximate solution of (4):

$$\xi = A' \cos 2\pi\omega_0' t + A'' \cos 4\pi\omega_0' t + \text{const.}, \tag{27a}$$

$$A' = A\left(1 + \frac{Ak_1}{3k}\right), \tag{27b}$$

$$A'' = A^2 k_1 / 6k, \tag{27c}$$

$$\omega_0' = \frac{1}{2\pi}\sqrt{k/m}, \tag{27d}$$

$$\omega_0 = \omega_0'\left[1 - \frac{5}{12}A^2\left(\frac{k_1}{k}\right)^2\right] \tag{27e}$$

In case the angular velocity is not zero, the molecule expands under the influence of centrifugal force, so that the equilibrium value of ζ changes from ζ_0 to ζ_1, where ζ_1 is a root of the equation

$$a\left(\frac{1}{\zeta^n} - \frac{1}{\zeta_0^n}\right) + \frac{m\Omega_0^2\zeta_1^4}{\zeta^3} - \omega \tag{28}$$

It is convenient to introduce the quantity $\Delta\zeta$ defined by the equation

$$\Delta\zeta = \zeta_1 - \zeta_0.$$

Expanding the left-hand member of equation (28) in series, neglecting terms containing the squares and higher powers of $\Delta\zeta$, and solving for $\Delta\zeta$, we obtain the approximate value

$$\Delta\zeta = \frac{m\Omega_0^2\zeta_0}{\dfrac{an}{\zeta_0^{n+1}} + 3m\Omega_0^2}.$$

By the introduction of the frequency of rotation ν, and by the use of equations (26a) and (27d) the above can be reduced to

$$\Delta\zeta = \frac{\zeta_0\nu^2}{\omega_0'^2 + 3\nu^2}.$$

Since the frequency of rotation ν is for all cases under consideration

[1] R. Seeliger, Verh. d. D. Physik. Ges., 16, p. 1042, 1914.

quite small compared with the frequency of vibration, we can neglect $\Delta\zeta^2$ in comparison with ω_0^2. Hence

$$\Delta\zeta = \zeta_0 \nu_r^2 \omega_0^{-2}. \tag{29}$$

Now let

$$\xi = \zeta - \zeta_1.$$

Expanding in series about the point ζ_1 and discarding higher order terms, we throw (24) into the form

$$m\frac{d^2\xi}{dt^2} = -\left[\frac{an}{\zeta_1^{n+1}} + \frac{3m\Omega_0^2\zeta_0^4}{\zeta_1^4}\right]\xi + \left[\frac{an(n+1)}{2\zeta_1^{n+2}} + \frac{6m\Omega_0^2\zeta_0^4}{\zeta_1^5}\right]\xi^2. \tag{30}$$

Let k' and k_2' denote the values of k and k_2 when Ω_0 does not vanish.

$$k' = \frac{an}{\zeta_1^{n+1}} + \frac{3m\Omega_0^2\zeta_0^4}{\zeta_1^4}$$

$$= \frac{an}{\zeta_0^{n+1}} + 3m\Omega_0^2 - \Delta\zeta\left[\frac{an(n+1)}{\zeta_0^{n+2}} + \frac{12m\Omega_0^2}{\zeta_0}\right].$$

$$k_2' = \frac{an(n+1)}{2\zeta_1^{n+2}} + \frac{6m\Omega_0^2\zeta_0^4}{\zeta_1^5}$$

$$= \frac{an(n+1)}{2\zeta_0^{n+2}} + \frac{6m\Omega_0^2}{\zeta_0} - \frac{\Delta\zeta}{\zeta_0^2}\left[\frac{an(n+1)(n+2)}{2\zeta_0^{n+2}} + 30m\Omega_0^2\right].$$

By means of further approximations and with the help of equations (27a), (27b), and (29) the above expressions for k' and k_2' can be reduced to

$$k' = 4\pi^2 m\omega_0^2\left[1 - (n-2)\frac{\nu_r^2}{\omega_0^2}\right], \tag{31}$$

$$k_2' = -\frac{4\pi^2 m\omega_0^2}{\zeta_0}\left[\frac{n+1}{2} - \left\{\frac{(n+1)(n+2)}{2} - 6\right\}\frac{\nu_r^2}{\omega_0^2}\right]. \tag{32}$$

Hence

$$k_2' k' = -\frac{n+1}{2\zeta_0}\left[1 - \left\{4 - \frac{12}{n+1}\right\}\frac{\nu_r^2}{\omega_0^2}\right]. \tag{33}$$

Let ω denote the frequency of vibration corresponding to the angular frequency ν_r. Then

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k'}{m}}\left[1 - \frac{5}{32}A^2\left(\frac{k_2'}{k'}\right)^2\right]$$

$$= \omega_0'\left\{1 - \frac{5}{48}\left(\frac{A}{\zeta_0}\right)^2(n+1)^2\right.$$

$$\left.\left[\frac{n-2}{2} - \left(8 - \frac{24}{n+1}\right)\frac{5}{48}(n+1)^2\left(\frac{A}{\zeta_0}\right)^2\right]\frac{\nu_r^2}{\omega_0^2}\right\}. \tag{34}$$

$$a = \frac{1}{\omega_0} \left| \frac{n}{2} - \frac{2}{3} \left(\frac{n}{2} - \frac{1}{2} \right) \frac{1}{2^2} + \frac{2}{5} \left(\frac{n}{2} - \frac{1}{2} \right) \left(\frac{n}{2} - \frac{2}{2} \right) \frac{1}{2^4} - \frac{3}{7} \left(\frac{n}{2} - \frac{1}{2} \right) \left(\frac{n}{2} - \frac{2}{2} \right) \left(\frac{n}{2} - \frac{3}{2} \right) \frac{1}{2^6} \right| \quad (38)$$

It is to be expected on the basis of the assumptions which have been made to formulate a law governing the motion of a system of which no two particles that n will have a value between 5 and 10. That being the case, it will be observed that for small values of β which is a measure of the amplitude of the vibration, a is a positive quantity whose value decreases with the energy of vibration. A qualitative agreement between the observed values of $\mathfrak{A}$ and $\mathfrak{A}'$ and the equations (20) and (21) or (22) is thus established.

The writer has shown elsewhere that in the case of H_2 the ratio A/ζ_0 should be in the neighborhood of 0.12 when $v = 1$. The above approximate equations are certainly not valid for such large amplitudes of vibration as this, but it is of interest to apply them even out of the range in which they are properly applicable.

The square of A is roughly proportional to the energy of vibration, which, in turn, is roughly proportional to v. Hence we may substitute $(0.12)^2 v$ for A/ζ_0 in (38). The observed values of $\mathfrak{A}$ and $\mathfrak{A}'$ are 8.65×10^{-14} and $2 \times 8.49 \times 10^{-14}$ respectively, from which we may assume, on the basis of equations (22), that 8.8×10^{-14} is not far from the correct value of $\omega(0, 0)$, or ω_0'. Substituting these values into (38) and giving n the value 7.5, we obtain

$$a = (3.125 - 0.0938 + 10^{-3}$$

Equations (22), based on the assumption that the vibrational energy may be reduced to zero, then give $\mathfrak{A} = 2.5 \times 10^{-14}$ and $\mathfrak{A}' = 5.7 \times 10^{-14}$. The observed values of these constants are $\mathfrak{A} = 2.55 \times 10^{-14}$ and $\mathfrak{A}' = 3.7 \times 10^{-14}$ respectively, so that the agreement is excellent. On the other hand it is not possible to choose any value of a which will give good values of either $\mathfrak{A}$ or $\mathfrak{A}'$ if we assume that equations (20) and (21) are correct.

The internal evidence of our theory therefore favors the hypothesis that for vibrational motion zero is one of the possible values of v. In other words, there is no "zero-point energy" for vibrational degrees of freedom such as that which the Bohr theory assumes for the rotational degrees of freedom. Too much weight should not be attached to this result, however, since the equations on which it is based are admittedly inaccurate and give excessively large differences between the frequencies N' and $2N$.

The problem of giving quantitative proof that the present extension of Bohr's theory is in harmony with Kirchhoff's law is substantially equivalent to the problem of deriving Planck's radiation formula from the theory in question, and it involves the introduction of hypotheses which are outside the scope of the present paper. The writer will therefore content himself here with a qualitative discussion of the relation of the theory to Kirchhoff's law in the hope that he may later have the privilege of taking up the problem in a quantitative manner.

Kirchhoff's law rests on the proposition that the ratio of the coefficient of emission of any medium for the frequency ν to its coefficient of absorption for the same frequency when in a state of thermodynamic equilibrium is equal to the specific intensity of black radiation for the same temperature and frequency divided by the square of the index of refraction.[1] If we assume (following in the footsteps of Planck) that we have to do with a gaseous medium of very low density, we may call the index of refraction unity. Denoting the coefficients of emission and absorption by ϵ_ν and α_ν respectively, and the intensity of black radiation by K_ν, we have

$$\frac{\epsilon_\nu}{\alpha_\nu} = K_\nu.$$

Let ν' denote any other frequency. Then

$$\frac{\epsilon_{\nu'}}{\alpha_{\nu'}} = K_{\nu'},$$

and by Planck's radiation law

$$\frac{\epsilon_\nu}{\epsilon_{\nu'}} : \frac{\alpha_\nu}{\alpha_{\nu'}} = \left(\frac{\nu}{\nu'}\right)^3 \left[\frac{e^{h\nu'/kT} - 1}{e^{h\nu/kT} - 1}\right]. \tag{36}$$

Equation (36) must be satisfied for any two frequencies ν and ν', if Kirchhoff's law is to be satisfied, and conversely we may apply (36) to the theory of harmonics as a test of its compatibility with Kirchhoff's law.

In making this test, we may, to begin with, neglect the broadening of the absorption and emission bands by molecular rotations and by the Doppler effect. ϵ_ν and $\epsilon_{\nu'}$ may then be replaced by the integrated intensities of the fundamental and harmonic emission bands, while α_ν and $\alpha_{\nu'}$ are replaced by the corresponding intensities of the absorption bands. It should be observed that if we replace ν' by 2ν the right-hand member of (36) decreases from infinity for very small values of the temperature T to one fourth for very large values of T. Consequently

[1] Cf. Planck's "Heat Radiation" (trans. by Masius), p. 35.

α, α_ν must increase to the same extent.

Now according to the writer's earlier theory of harmonics the rati of the intensities of the fundamental and harmonic bands was inde pendent of the temperature for both the absorption and emission pro cesses, in complete disaccord with (36). The present theory, on th other hand, provides for a large temperature variation in the relativ emission from the two bands, although the ratio of the absorption per centages should be independent of the temperature. This is becaus the fundamental and harmonic emission bands have their origin in *different* groups of molecules, the relative numbers in which vary with the temperature. Thus, at the lowest temperatures the number of molecules in the second steady state is infinite compared with the number in the third, while at extremely high temperatures the numbers approach equality and the *relative* intensity of the fundamental emission band decreases correspondingly.

The above fact establishes a qualitative agreement between our new theory of harmonics and Kirchhoff's law and shows that the new theory meets all the difficulties encountered by the old in a qualitative manner, at least. It should be observed, however, that there is a minor contra- diction to Kirchhoff's law involved in the Bjerrum theory of the struc- ture of the infra-red absorption and emission bands upon which the present work is in part based. For if we let ν and ν' in equation (36) denote the frequencies of the two quantum lines in one of these bands which are due to the group of molecules having any one of the possible angular velocities, we get into the same trouble as in the writer's first theory of harmonics. The two elementary absorption bands are due to the same group of molecules and the two emission bands are due to the same group. Consequently the ratio of the intensities of the absorption bands and the ratio of the intensities of the two emission bands should apparently each be independent of the temperature. As the Bjerrum theory is very well established the above consideration seems to force the conclusion that, while equation (36) may be, and probably is, correct when applied to regions of the spectrum which are far apart, it cannot hold when applied to narrow strips of the spectrum which are very close together. In other words, Kirchhoff's law and the rule that the ratio of the intensity of radiation inside any body or substance in thermo- dynamic equilibrium to the square of the index of refraction is a uni- versal function of the temperature and frequency, while approximately correct as broad generalizations, are not strictly true when applied to the comparison of closely adjacent portions of the spectrum.

Since placing the above paper in the hands of the publishers, my attention has been called to the formulation of the quantum condition for the determination of the steady states of motion by W. Wilson (Phil. Mag., 29, pp. 795–802, June, 1915), and the arrival of the long delayed copies of the Annalen der Physik for 1916 has put into my hands the independent formulation of this same hypothesis by Sommerfeld, together with his brilliant explanation of the complex structure of the lines in the spectra of hydrogen and ionized helium by its aid.

The quantum condition in question takes the form of the requirement that certain of the generalized coördinates of the atomic or molecular systems in question shall satisfy equations of the form

$$\int p dq = nh,$$

where p is the momentum corresponding to the coördinates q, h is Planck's constant, n is an integer, and the integration is to be extended over a complete cycle of values of q. Applying this condition to the vibration of a diatomic molecule we obtain

$$\int m\dot{s}\,ds = 2\int T dt = nh,$$

or

$$T = \frac{n}{2} h\omega.$$

Here, as in the text above, T and ω denote the kinetic energy and the vibrational frequency respectively.

If we assume, as a first approximation, that the mean values of the kinetic and potential energies are sensibly equal, we obtain equation (1) above.

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HELIUM AND HYDROGEN MODELS

To the EDITOR OF SCIENCE: In a communication to the SCIENCE issue of June 18 Dr. Irving Langmuir proposed a model of the helium atom consisting of a nucleus of charge 2e accompanied by a pair of electrons which execute symmetrical oscillations about two nearly circular arcs on opposite sides of the nucleus. In the issue of November 5 he has proposed a similar model for the hydrogen molecule, and another, of a somewhat different type, for the positively charged H_2 ion. The writer was particularly interested in these models, for in each case the resultant angular momentum is zero, a circumstance which seemed to offer an explanation of the diamagnetic behavior of helium and hydrogen, and of the failure of the theories of the specific heat of hydrogen based on the assumption that the molecule is gyroscopic.

Unfortunately, Dr. Langmuir did not see how to apply the Wilson-Sommerfeld quantum conditions to the determination of the energies of these models, and therefore was not able to fix the theoretical energies and ionization potentials definitely. These quantum conditions are

$$\begin{aligned} \int p_1 dq_1 &= \int \left(\frac{\partial T}{\partial \dot{q}_1}\right) d q_1 = n_1 h, \\ \int p_2 dq_2 &= \int \left(\frac{\partial T}{\partial \dot{q}_2}\right) d q_2 = n_2 h, \\ &\cdots\cdots\cdots\cdots, \end{aligned} \tag{1}$$

where T is the kinetic energy of the atom or molecule, q_1, q_2, ... are a properly chosen set of coordinates, p_1, p_2, ..., are the corresponding momenta, and n_1, n_2, ... are any integers.

[illegible] integral is to be extended over a complete cycle of values of the corresponding coordinate. Dr Langmuir states that he is unable to apply these equations to his problem because he does not know what system of coordinates to use. The choice of a proper coordinate system is not essential, however, to the application of these conditions to the type of problem under consideration. For whatever coordinates are used, they will have a common period t, which makes possible a convenient combination of the conditions. The set of equations (1) can be written in the form

$$\int_0^t \frac{\partial T}{\partial \dot{q}_1} \dot{q}_1 dt = n_1 h,$$

$$\int_0^t \frac{\partial T}{\partial \dot{q}_2} \dot{q}_2 dt = n_2 h, \qquad (2)$$

Adding, we obtain

$$\int_0^t \left[\frac{\partial T}{\partial \dot{q}_1} \dot{q}_1 + \frac{\partial T}{\partial \dot{q}_2} \dot{q}_2 + \quad \right] dt = n_1 h + n_2 h + n_3 h \quad (3)$$

By Euler's theorem for homogeneous functions, the integrand of the left hand member is equal to twice the kinetic energy. Consequently this integral is equal to the action of the system for the type of motion under consideration. Denoting the sum of the integers n_1, n_2, etc., by n, we have

$$A = \int_0^t 2T dt = nh, \quad n = 0, 1, 2, \ldots \qquad (3)$$

This integral is invariant of the choice of coordinates and can be evaluated easily if the orbit and potential energy function are known. Equation (3) is not equivalent to the quantum conditions (1), but it is a deduction

[1] With the exception of the positive H, ion. He does apply the conditions to this model, and correctly, but expresses doubt concerning the validity of the somewhat unsatisfactory result on account of his uncertainty regarding the coordinate system

from them for the type of problem under consideration, which is sufficient to fix the possible energy values of the atom or molecule. In the normal state the atom will have the least energy possible and the quantum number n should therefore be small, though the value zero must be ruled out if there is to be any dynamic equilibrium at all. In the case of the helium atom or the hydrogen molecule, it is to be expected that n will be either one or two.

I have carried through the numerical evaluation of the action integral for the helium atom model and regret to say that the calculation shows that if the atom is given an energy corresponding to its ionization potential, the quantum condition (3) is *not* satisfied.

In making the calculation I have used an approximate expression for the path of the electron. This is permissible, since, by the principle of least action, the variation in the integral produced by a small variation in the path, holding the total energy constant, vanishes to small quantities of the first order. The determination of the approximate path was based on the data furnished by Dr. Langmuir. He says that the path of each electron is very nearly an arc of an eccentric circle subtending an angle of 155° 56′ at the nucleus. The radius vector from the nucleus to the midpoint of the orbit is 0.2534×10^{-8} cm. for an ionization potential of 25.59 volts, and the radius vector at the end of the orbits is 1.138 times as great. By expanding the expression for the radius vector into a power series in θ (the angle between the momentary radius vector and the radius vector to the midpoint), and discarding higher power terms, it is easy to show that an equation of the form

$$r = r_0(1 + k\theta^2) \tag{4}$$

can be used to define an approximate orbit. Here r_0 is 0.253×10^{-8} cm. and k is easily

calculated from the known values of r and θ at the end of the path.

The expression for the potential energy of the system is

$$\phi = -\frac{2e^2}{r} + \frac{e^2}{2r\cos\theta} \qquad (5)$$

where e is the charge on the electron. The total energy H is easily calculated from the above equations by inserting the values of r and θ for the end of the path. The kinetic energy of the two electrons is

$$T = H - \phi = mv^2 \qquad (6)$$

By means of equations (5) and (6) the expression for the action is easily transformed into the form

$$A = 4\int_0^{s_m} 2mv\,ds$$

$$= 8\sqrt{m}\int_0^{s_m}\sqrt{\frac{4}{r} - \frac{1}{2r\cos\theta} - \frac{H}{e^2}}\,ds, \qquad (7)$$

where s is the rectified length of the path from its midpoint to the point (r, θ), and s_m is the maximum value of s. The graphically determined value of the integral which forms the right hand member of (7) is 15.5 h. This result is in conflict with the quantum condition (3) and shows that if the quantum conditions (1) are correct, the Langmuir model of the helium atom will not account for the observed ionization potentials of that element.

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A HELIUM SERIES IN THE EXTREME ULTRA-VIOLET

It has been shown that the helium series first discovered in a terrestrial source by Fowler can be represented by the formula

$$\nu = 109{,}750\left(\frac{1}{\left(\frac{n_1}{2}\right)^2} - \frac{1}{\left(\frac{n_2}{2}\right)^2}\right);$$

where n_1 has the value of 3 or 4[1]

If n_1 be given the value 2, and n_2 the successive value 3, 4 and 5, lines result at wave-length 1640.1, 1214.9 and 1084.7. My previous investigations of the helium spectrum did not afford much evidence as to the existence of these lines,[2] a recent search, however, has been more successful. With a powerful disruptive discharge in helium, a sharp, fairly strong line appears at 1640.3; no trace of it is found in hydrogen under the same electrical condition and it does not occur in helium when the discharge circuit is free from capacity. Under the same violently disruptive condition the line at 1216, always present in helium and hydrogen, develops a satellite on its more refrangible side, this satellite is not well resolved, but its wave length appears to be about 1215.1. The region that should be occupied by 1084.7 is obscured by a strong pair at 1085, probably due to an impurity.

Owing to the difficulties of vacuum spectroscopy it is perhaps unwise to claim that the evidence in this case is conclusive. I regard it as very probable, however, that two members of this series in helium have been found in the extreme ultra violet.

THEODORE LYMAN

HARVARD UNIVERSITY,
October 25, 1919

[1] Evans, *Phil. Mag.*, 29, p. 284, 1915.
[2] *Astrophys. Jour.*, 43, p. 92, 1916.

THE SPECTRUM OF HELIUM IN THE EXTREME ULTRA VIOLET.

By Harold Jacoby and Theodore Lyman.

The study of the Spectrum of Helium in the Schumann region, which was published some five years ago, yielded results which were difficult to interpret,[1] and the conclusions drawn from a more recent attack on the same subject,[2] though interesting, were by no means final. Both investigations suffered from the same defect, for to obtain any lines at all when helium was used in the vacuum tube it was necessary to employ a strong disruptive discharge, an electrical condition sure to introduce impurities by its action on the walls of the tube and upon the electrodes.

The upshot of the whole matter was that, though the region between 1700 and 1200 Å.U. contained a considerable number of lines, only those at 1640 and 1215 could be attributed to helium.[3] It has been pointed out that these wave-lengths fit the relation $\nu = 4N\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$, and therefore probably form members of the enhanced spectrum series. Even now, however, the origin of these lines cannot be regarded as perfectly certain.

It has become increasingly evident during the progress of the present investigation that the arrangement proposed by Hicks[4] by which a considerable number of lines, many of them certainly due to impurities, were made to fit the formula for the enhanced spectrum, is without justification.[5]

The immediate cause of the renewal of the attack on the problem was the discovery by several investigators of a resonance potential in helium corresponding to a wave-length of about 600 Å.U.[6]

[1] T. Lyman, Astrophysical Journal, xlvi No. 2, p. 89 (1916).
[2] T. Lyman, Science, xlv p. 187, Feb. 1917.
[3] T. Lyman, Nature, xcv p. 314 (1919).
[4] Hicks, Nature, xcv p. 193 (1919).
[5] T. Lyman, Nature, xcv p. 563 (1920).
[6] F. Horton & A. C. Davies, Proc. Roy. Soc. xcv p. 408 (1919). F. Horton & D. Bailey, Phil. Mag. xl p. 440 (1920). J. Franck & P. Knipping, *Phys. Zeitsch.* xx p. 481 (1919). *Zeitsch. f. Physik*, i p. 320 (1920). K. T. Compton, Phil. Mag. xl p. 553 (1920).

the employment of a vacuum spectroscope with a grating of 30 cm radius the gas also quite soon greatly reduced and even by the use of a continuous current of helium the impurities

The result of these experiments was the discovery of a fairly strong line at 584 A U. The existence of this helium line was confirmed by an observation with the vacuum grating spectroscope of 97 cm radius long used in this laboratory.

It is interesting to note that the ionization potential corresponding to 584, 21.2 volts, agrees rather with the results of Franck and Knipping than with those of other investigators. The significance of this fact will be considered presently.

It may be concluded that, apart from the two lines already mentioned as probably belonging to the enhanced spectrum, but whose origin is even now somewhat doubtful, only one line in the extreme ultra-violet can be ascribed to helium with any certainty at present.

The description of the experimental arrangements and a detailed discussion of results follows.

The vacuum spectroscope containing the grating of 30 cm radius was so arranged that its joints could be closed with Khotinski cement. This method of sealing together with the small volume facilitated the production of an excellent vacuum, and assisted in preserving the purity of the gas under examination. The discharge-tube was of quartz, the cathode being of aluminum and cylindrical in form, about 2.4 cm long with a hole 5 mm in diameter, the anode was of tungsten. The cathode was always placed at the end of the tube near the slit. The helium was purified by charcoal and liquid air, the spectroscope being protected from mercury vapor by U tubes refrigerated in the usual manner. The gas when originally prepared was free from impurities. However, as it was impossible to heat the whole apparatus, the helium not infrequently showed the presence of traces of hydrogen and the oxides of carbon when examined after it had been admitted to the spectroscope.

The gas was usually at a pressure of eight tenths of a millimeter, the current being between twenty and forty milliamperes.

The dispersion of the grating was 84.6 A U. to the mm., the region contained in the length of the photographic plate extending from the slit image to the neighborhood of 1200 A U.

at 585 A.U. is the intensity bears a constant ratio to that of the direct image of the slit. The other lines which are usually present at 680, 860, 972, 992, 1020, and 1176 show varying relative intensities, none of them occurring on all our plates. Their behaviour indicates that they are due to impurities. The conclusion is confirmed by the fact that we have found lines at 686 A.U., 860, and 1176 when we employed a high potential vacuum spark between carbon terminals with our small spectroscope. Millikan[1] has obtained radiations from the same source at nearly identical wave lengths, namely 687.3, 858.6, and 1175.6, using a grating of greater dispersion than ours. The line 992 has already been attributed to an unknown impurity.[2] 972 and 1020 are due to hydrogen.[3]

Hicks[3] has suggested that as the lines 972, 992, 1020, and 1086 fit the formulæ for the enhanced spectrum of helium, they must belong to that gas. The fact that the line 1086 is not found on our plates is sufficient in itself to disprove this idea.

When we undertook to confirm our observations by means of the large spectroscope, it was only after several trials and with a very long exposure that we were able to obtain a faint but unmistakable record of λ 585. It was accompanied by fairly strong lines at 1216, 1200, 1026, and 1085, all of which have been observed before with the same instrument and are known to belong to hydrogen or to some other impurity. In the visible spectrum the discharge showed traces of hydrogen and carbon in about the same intensities as when the small spectroscope was used. In addition, nitrogen bands appeared very faintly at the end of the exposure. The impurity, not present with the smaller grating, may account for the appearance of the lines at 1200, 1086, and 1085. The region covered by the photographic plate extended from 500 to 1300 A.U.

Owing to its faintness and to the fact that it was separated from lines of reference by a considerable distance, an exact measurement of the wave length of this resonance line is impossible at present, however, the value of 585 ± 2 may be regarded with confidence.

The feeble character of λ 585 may be attributed to the long gas path of the large spectroscope whose grating has a radius of cur-

[1] R. A. Millikan, Astrophysical Journal, 53, p. 47 (1920).
[2] T. Lyman, Astrophysical Journal, this No. 2, p. 89 (1919).
[3] Hicks, Nature, 104, p. 181 (1919).

struction. If we are willing to assume [illegible] absorption by helium in the neighborhood of the line in question. This hypothesis of selective absorption is made necessary by the fact that a disruptive discharge in helium connected with the [illegible] spectroscope visibly strong impurity lines of electron energy less than λ 585.

It may appear curious that this resonance line was not discovered in previous researches where a disruptive discharge was employed. This may be explained in two ways. First on the ground that the impurities known to be liberated by the disruptive discharge carry the current to the exclusion of the helium second, by reference to the work of Compton, Lilly and Chaston on the minimum arcing voltages in which they have shown that when current density is high it is possible to obtain an arc at about 8 volts with the emission of the ordinary helium spectrum while the resonance potential line requires upwards of twenty volts. It would seem, therefore, that with high current densities it might be quite reasonable to expect a bright helium spectrum in the visible spectrum without the resonance line in the extreme ultra violet.

In conclusion, it is interesting to note that if we follow the speculations of Bohr, Sommerfeld[2] and others,[3] two resonance potential lines in helium might be expected corresponding to the two principal series of this element. The wave numbers of the limits of these two principal series are respectively 438511 and 38453, these figures corresponding to potentials of 4 0 and 4 8 volts. Taking the ionization potential of helium as 25 2 volts and subtracting from it the values 4 0 and 4 8, we obtain the values 21 2 and 20 4 as the two values of the resonance potentials in helium. The line 585 corresponds to the value 21 2 that we have only this line in the spectrum and not the line corresponding to 20 4 volts appears to agree with the work of Franck and Knipping.

Jefferson Physical Laboratory,
Harvard University,
December, 1920

[1] K. T. Compton, E. T. Lilly, & P. S. Olmstead, Physical Review, [illegible] p. 282 (1920). Compare T. C. Hebb, Phys. Rev. xvi p. 173 (1920).
[2] Sommerfeld, *Atombau u. Spektrallinien*, 2nd Ed. p. 287.
[3] J. Franck & P. Knipping, *loc. cit.*

Lick Observatory Bulletin, Vol. II, No. 1. January 1920

REVISION OF THE SERIES IN THE SPECTRUM OF BARIUM

By H. A. SAUNDERS

ABSTRACT

Spectrum of barium: series of triplets and single lines. The spectrum of barium contains three systems of series, the triplets, the single lines, and the pairs. After making a careful study of all available data, including recent unpublished observations by King, the author has revised and extended the previously recognized series of triplets and single lines and has identified the lines corresponding to one or more terms of each of several other series. Altogether about 145 lines are assigned to one or other of various series, with 8 principal series of triplets, eight series of single lines, and two other subordinate combination series. Accurate constants for these series are given. The fundamental and diffuse series of triplets are unusually complex, and these and other series show a curious merging action both in the relative intensities of the terms and in the wave lengths. No simple formula of the ordinary type will give the frequencies accurately. The paper includes a brief *explanation of the notation* used in designating the different series.

Recent experimental work has led to a considerable extension of our knowledge of the spectrum of barium. A. S. King[1] published some excellent measurements from plates covering the visible and ultra violet portions of the spectrum, using a vacuum furnace as source. Since then he has extended the range of these photographs into the ultra red and taken several plates especially to help in working out the series in this spectrum. All these he has generously turned over to me for study, and the results are here given. If they are of value, the credit should be given to Dr. King.

H. M. Randall[2] has made a careful study of the ultra-red, and Meggers[3] and Eder[4] have helped to fill in a gap between the visible and the ultra red. Mention should also be made of the dissertations of Schmitz,[5] George,[6] Lorenser,[7] and Werner.[8]

[1] *Astrophysical Journal*, **48**, 11, 1918. [2] *Astrophysical Journal*, **42**, 195, 1915.

[3] *Scientific Papers*, No. 311, Bureau of Standards, 1918.

[4] *Wiener Ber.*, **123**, IIa, December 1914.

[5] *Zeitschrift für wissenschaftliche Photographie*, **11**, 309, 1913.

[6] *Ibid.*, **13**, 121, 1913. [7] Tübingen, 1915.

[8] *Annalen der Physik*, **44**, 189, 1914.

All these new observations have helped to fix the system of series in this spectrum with more certainty, and the present paper contains an accurate set of constants connected therewith as well as several new series. A similar study of the spectra of Ca and of Sr, not yet quite finished, makes it possible to settle the nature of certain series in Ba on account of the close analogy with these spectra. The writer has also derived assistance in this task from some observations by S. Popow, made in the laboratory at Tübingen in the winter of 1913–14 under Paschen's direction on the Zeeman effect in Ca, Sr, and Ba. These have not yet been published in full, but were used by Popow as the basis of one article.[1]

The full spectrum of Ba consists of three systems of series. Each system contains at least four different types of series, and there are combination series derived from these. The present paper is for the purpose of revising the series in the triplet and single-line systems; the pair system is large and important, but is reserved for a future communication.

The results are given in the form of a set of tables, one for each series, with explanatory notes. The notation used has been explained earlier,[2] and is almost identical with that used by Paschen. A brief explanation is here repeated. The best series formula is probably of the type

$$\frac{1}{\lambda} = \nu = L - \frac{N}{(m + a + K)^2},$$

where N is the so-called series constant, approximately constant for all elements; L is the limit of the particular series in question; m is the variable integer; a is a constant peculiar to this series; K is a "residual," which is itself a function of m and of other constants, which diminishes rapidly toward zero for the outer lines of a series (m large). In Rydberg's formula K is zero, in the formula of Mogendorff it has the value $\frac{b}{m}$; but these simple values are by no means generally applicable.

The fraction $\frac{n}{(m+a+K)^2}$ is called the "term," and is accurately known for any series as soon as the limit is found. The terms are

[1] *Annalen der Physik*, 45, 147, 1914.

[2] *Astrophysical Journal*, 41, 373, 1915.

represented by the symbols $m(p)$, (ms), (md), and (mf) in the four types of series, the principal, sharp, diffuse, and fundamental, in the triplet system, $m[P]$, (mS), (mD), (mF), likewise, for the single line system.

TRIPLET SERIES SYSTEM

"Fundamental" or narrow series of triplets, $(1d)-(mf)$. This is now the most accurately measured series in Ba, due to the sharpness of the lines in the vacuum furnace, and the excellent results of King. On this account it is mentioned first. The list here given includes a few very faint lines not given in King's paper, but measured since then from his plates, either by him or by the writer. This series was first suggested some time ago[1] and three of its triplets correctly identified. The course of the rest of the series as then suggested proved, however, to be incorrect and was difficult to settle, chiefly because the second member of the series is abnormally

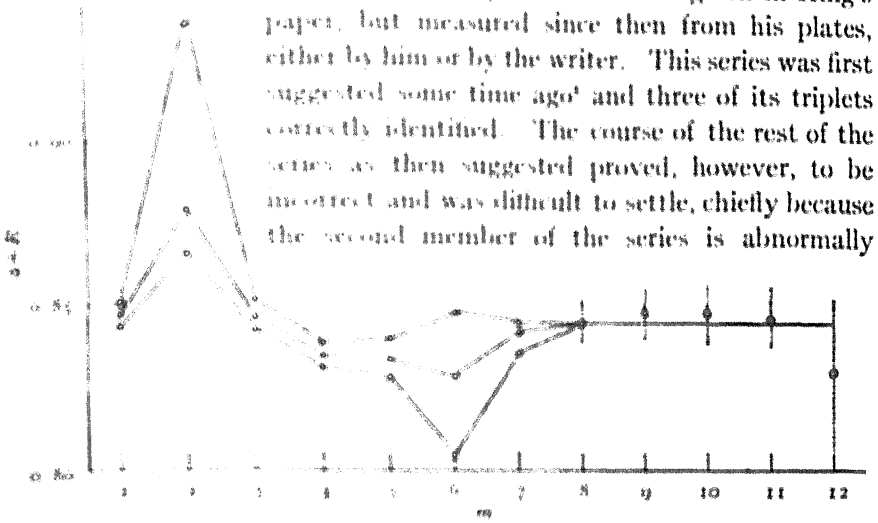


FIG. 1. Variation of $a+R$ with m. Dotted lines show estimated errors

faint. Unwilling as one might well be to admit the possibility of series in which the intensities run abnormally, there is now no doubt that they occur. Lorenser was not deterred by the abnormality referred to, and suggested an arrangement for the series which proves to be much nearer the truth. His second member is, however, wrong.

The series is complex, as are the corresponding ones in Ca and Sr, a feature which is, so far, rare in series of this type. It is, moreover, curiously irregular. In order to exhibit this irregularity three curves are given (Fig. 1), showing how the quantity $a+R$

[1] *Astrophysical Journal*, **28**, 118, 1908.

$(id_1) = 32433.0$
$(id_2) = 32814.1$
$(id_3) = 32095.6$

λ	σ	$\Delta\sigma_1$	λ	σ	$\Delta\sigma_1$	λ	σ	Terme m'	$m' \cdot \delta \cdot \beta$
3997.92	25006.1	381.2	3937.86	25387.3	381.5	3909.93	25768.8	7405.4	1.4746
95.66	020.2	381.0	35.72	402.2				7423.7	1.4784
93.40	054.4	.....						7442.0	1.4822
3396.33	27798.3	381.2	3347.70	28179.5	381.6	3318.97	28560.1	6474.1	1.4384
93.20	833.7	380.9	44.66	202.6				6492.4	1.4422
79.67	927.7	.....						6510.7	1.4460
3421.48	29218.9*	381.4	3357.39	29600.2	381.5	3326.60	29981.7	3351.1	1.4746
21.01	222.9	381.0	56.96	982.5				3369.4	1.4784
20.32	326.8	.....						3387.8	1.4822
3373.06	30098.5	381.0	3322.17	30479.8	380.8	3295.20	30860.4*	3351.1	1.4746
72.20	099.5		21.10	479.5				6.4	
								6.4	
3349.80	30978.2*	380.7	3322.44	31359.0	380.8	3295.43	31739.7	3369.4	1.4784
96.12	978.2		22.39	358.9*				3387.8	1.4822
								3406.2	1.4860
3325.68	31857.0*	380.7	3299.44	32237.7	380.8	3272.43	32618.5	3387.8	1.4822
74.16	857.0		00.13	237.7				3406.2	1.4860
								3424.6	1.4898
3301.56	32736.7*	380.7	3276.13	33116.5	380.8	3249.12	33497.3	3406.2	1.4860
52.04	736.7		77.82	116.5				3424.6	1.4898
								3443.0	1.4936
3277.44	33616.4*	380.7	3252.81	33995.2	380.8	3225.80	34376.0	3424.6	1.4898
29.92	616.4		54.50	995.2				3443.0	1.4936
								3461.4	1.4974
3254.32	34496.1*	380.7	3229.49	34874.8	380.8	3202.48	35255.6	3443.0	1.4936
07.80	496.1		31.18	874.8				3461.4	1.4974
								3479.8	1.5012
3231.20	35375.8*	380.7	3206.17	35754.5	380.8	3179.16	36135.3	3461.4	1.4974
3208.08	35255.5*	380.7	3182.85	36634.1	380.8	3155.84	37014.9	3479.8	1.5012
3184.96	36135.2*							3498.2	1.5050
3161.84	37014.9							3516.5	1.5088

TABLE II

[illegible] SERIES OF TRIPLETS [illegible]

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4493.66 4489.09	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
4087.51 4084.87	24459.3† 473.8	878.3	3947.53 3945.40	[illegible]	570.6	[illegible]	[illegible]	[illegible]	4
3898.58 .... 3894.34	25643.3 671.0	878.2	3773.93 3760.48	26504.3 26532.3	570.6	3719.93‡	[illegible]	[illegible]	5
3789.72 .... 3788.18	26379.89 390.6	878.2	3667.93 3667.60	27255.7 27258.1	....	§	....	2124.2 2134.8 2137.1	6
3721.17 .... 3720.85	26865.7 26868.0	878.0	3603.40	27743.7	....	....	....	1646.8 1649.1	7

* Measured by Randall. This whole triplet occurs inverted in position. On this account in calculating its "terms" its frequency is to be taken as negative.

† Probably there is a diffuse series line at ν 24459.4 and a sharp series line at ν 24459.1; not resolved.

‡ King's plates show an iron line at 3719.93 from which the Ba line here given cannot be separated, when both are present. In one photograph, when a very small quantity of iron was present, this line showed unusual strength, and was then doubtless largely or entirely due to Ba.

§ King's plates show an iron line at λ 3618.77 which covers the faint Ba line to be expected there, due at 3618.72.

varies with m for each of the three lines which together constitute the first "line" of each triplet. The curves show that K must be a complex function of m, or else that the term type of formula is quite different from that now accepted. They show moreover, how curiously the structure of the triplet groups appears and closes again in passing along the series. The existence of the constant frequency differences makes it necessary to regard these abnormalities as real. Others of the same sort occur in Ca.

Diffuse or first subordinate series of triplets, $(1p)-(md)$. The diffuse triplet series has been extended by one term and the accuracy of all wave-lengths greatly improved from King's plates. The limit used here was obtained indirectly from the fundamental series, for greater accuracy. The curve of residuals for this series, though very far from complete, shows an abnormal course as far as it goes.

Sharp or second subordinate series of triplets, $(1p)-(ms)$. King's plates show a few new lines of this series. The presence of bands makes it difficult to follow the series farther out.

TABLE III

SHARP SERIES OF TRIPLETS, $(1p)-(ms)$

$(1p_1)-28.134$ *

$(1p_2)-29.192$ *

$(1p_3)-29.763$ *

h	ν	$\Delta\nu$	h	ν	$\Delta\nu$	h	ν	Intensity	m
7901.80	12645.5	0.5	7291.44	13712.1	57.6	6932.48	14421.6	2	4
4607.90	21710.5	0.5	4555.42	21956.7	57.6	4504.38	22198.9	2	5
4239.18	23586.9	0.5	4207.24	23768.1	57.6	4176.59	23951.7	1	6
3975.31	25154.8	0.5	3948.45	25320.6	57.6	3921.62	25505.2	1	7
3808.93	26251.0	0.5	3784.43	26420.0	57.6				8

* See Table II, second note.

† The last triplet is presented tentatively, as its faintness makes it very difficult to separate it from the bands which are present.

Principal series of triplets, $(11)-(mp)$. This series is new and very incompletely observed. It is very faint and lies in the ultra-red. It forms combination series (see below) which are analogous to others in Ca and Sr; it is only by means of these that its course can be settled. The first triplet in the table belongs, in a mathematical sense at least, to this series, but is, physically speaking,

the first triplet of the sharp series. The third triplet cannot yet be checked by calculation from any combination and must be regarded as only provisionally located.

TABLE IV

Principal Series of Lithium, $(1S) - (mP)$. $(1S) = 15869.3$

λ	ν	$\Delta\nu$	λ	ν	$\Delta\nu$	λ	ν	Terms (mP)	m
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	12615.5	28514.8	1
								29192.8	
								29703.3	
	6707.8	73.6		6703.3	174.3		4836.8	11042.5	2
	6703.3	73.6			174.3		calc.	11214.0	
			3232.7	6703.3	174.3	10214.0	4827.0	11280.4	
			obs.	obs.	obs.	obs.	obs.		
4132.0	24191.8*	141.0	3232.7	6703.3	80.1	10189.1	9812.1	6057.2	3
								6117.3	
								6180.9	

* Recently found by Marshall.

SINGLE LINE SERIES SYSTEM

Principal series of single lines, $(1S) - (mP)$. This series has proved to be unexpectedly difficult to work out. After the corresponding series in Ca and in Sr were found, it was evident that

TABLE V

Principal Series of Single Lines, $(1S) - (mP)$. $(1S) = 42029.4$

λ	ν	Terms (mP)	m
5535.53	18060.2	23969.2	1
5077.59	19687.7	24341.7	2
4727.63	21153.9	20875.5	3
4593.68	21764.1	20265.3	4
4343.5	23018	19011	5
4130.2	24207*	17822	6
3933.8	25423*	16606	7

* Not positively identified as belonging to this series.

this series should occur in Ba also, and should begin with the flame line λ 6141. In an earlier article[1] I remarked that λ 2597 had exactly the right aspect for a member of this series. Later on,[2]

[1] *Astrophysical Journal*, **35**, 135, 1912.

[2] *Physical Review*, **1**, 331, 1913. The series SL.1 suggested at that time has proved, in the light of more accurate data, to be incorrect.

I gave the arrangement of the beginning of the series. Recently McLennan and Young[1] using the method of reversal of the lines by the vapor of the metal which had long been known to be useful in picking out lines of series of that type, have obtained a successful photograph clearly showing the later lines of the series. They also calculated the limit approximately. Their choice of lines for the series differs somewhat from mine. Lines include, for instance, two lines λ 2237 and λ 2894 for whose existence there is no other evidence. This region has been gone over very carefully by several observers, including King, who uses a furnace as source in which this series must surely appear complete, and in which, in fact, its first line is relatively stronger than usual. High precision is, of course, not claimed for their wave lengths quoted above, but the known line nearest to λ 2894 is ten units away, and one must therefore suppose either that there was some error in identification in this case, or else that in a source particularly favorable to this series, and in which some of its lines are enhanced, others fail to appear. The latter assumption seems to me quite untenable.

The course of the series as suggested in the table receives support from the discovery of combination series derived from it, and presented below. The limit of the series has been accurately fixed by means of one of these, $(1S) - mf_2$, a combination between this series and the principal series of triplets.

The series is abnormal in the same sense that the fundamental series of triplets is abnormal, that is, the curve of residuals is not a simple one, and no simple formula will fit the series. The outer lines have not yet been measured with satisfactory precision, and therefore the full curve cannot yet be traced.

Diffuse series of single lines, $(1P') - (mD)$. The experimental evidence necessary for the isolation of the lines of this series is still far from complete. Its limit $(1P')$ is known from the principal series. The first term $(1D)$ is probably 30614.1, a conclusion which is reached by the considerations which follow. There are several pairs of lines in the Ba spectrum with a frequency difference of 11395.3 and one line of each of these belongs to a series

[1] *Proceedings of the Royal Society*, **94**, 425, 1919.

ending at $1S_0$ or 14550.4. This indicates the existence of shifted series ending at $14550.4 + 11604.6$, or 26154.1. If this number is then a limit of one of more series, it must itself be a term of some other series. It cannot be a term of the sharp series, for $(2S)$ would be far smaller. The same can be said for the fundamental series. It must therefore belong to the diffuse series and be the term $1D$. In this case one of the series ending at this limit is probably the fundamental series, and this is given below.

Having fixed the value of $(1D)$, the difference $(1P)-(1D)$ should give the first line of the diffuse series. $(1P)$ is 23969.2, and therefore the difference is a negative quantity. The occurrence of negative frequencies is not uncommon in series, but has not before been suggested for any diffuse single-line series. It occurs in others, however, e.g. in the diffuse series of pairs and of triplets in the Ba spectrum. Besides, in all sharp series, the first member is also the first member of the principal series, one of these being taken with a negative frequency, thus giving a close relationship in all elements between the series $(1S)-(mP)$ and the series $(1P)-(mS)$. In the spectrum of Ba, and also in Ca and Sr, there exists this same relationship between $(1D)-(mP)$ and $(1P)-(mD)$. The former of these two is the series formerly called S1, 2, which is given for Ba below, as a combination series of principal type in the single line system.

The difference $(1P)-(1D)$, ignoring the sign, leads to 6664.9, which hits a line of some strength, observed by Randall in the ultra-red. This is therefore at once the first line of the diffuse series and of the combination series. The term $(2D)$ can be predicted by a formula but not exactly; it indicates that the next line of the diffuse series is in the ultra red, but further experiments are needed to settle this line exactly and to fix the others in the series. The rest of the series may, for instance, include $\lambda\lambda$ 9831.7, 6233.59, 5367 (0), 4877 (0), and 4663 (0), and, if so, the combinations $(1p_1)-(1D)$ and $(1S)-(3D)$ appear to exist; but there is no definite evidence on hand on which to decide whether this selection is correct or not. Observations on the Stark effect in Ba should reveal this series, since it appears that diffuse series are as a class sensitive to the effects of electric fields.

Sharp series of single lines $(1P) - (mS)$. Both $(1P)$ and $(1S)$ being known, it ought to be possible to guess at $(2S)$ by means of a formula without much ambiguity, but there are many lines in the expected region, the ultra-red, and the true one cannot be settled in this way alone. The term $(2S)$ is, however, very likely to occur in combinations, such as $(2S) - (2S)$, $(2S) - (mP')$, and perhaps others. I have found that if we assume $(2S)$ to have the value of 16400.4, as it well may, according to any reasonable formula, then we get

$(1P) - (2S) = 7468.8$ calc., 7469.8 observed as a strong line by Randall.

$(1S) - (2S) = 25029.6$ calc., 25031.6 observed as a faint line.

$(2S) - (3P) = 11560.9$ calc., 11560.9 observed as medium line.

$(2S) - (4P) = 12870.6$ calc., 12871.8 observed as a weak line.

As these agreements are good, I feel that they are probably correct, and, if so, $\lambda\,14307$ (*v* 7000.8) is the sharp series line in the ultra-red. The next line of this series cannot be picked out with certainty at present. There are several possible lines in the likely region.

Fundamental series of single lines $(1D) - (mF)$. As explained above, there are two series ending at the limit $(1D)$, and one of

TABLE VI

FUNDAMENTAL SERIES OF SINGLE LINES. $(2D) - (mF)$. $(2D) - 5066.34$.

λ	ν	Terms (mF)	m
5826.29	17158.9	11471.5	3
4080.93	24497.4*	6132.9	5
3789.74	26392.7†	4238.6	6

* This line is almost exactly $(4D) - (5F)$, but as $(4D) - (5F)$ does not occur this must be regarded as an accidental coincidence.

† This line almost coincides with a line of $(5P) - (mS)$, of a doubtful which one was measured, or a blend of both.

these is of a new type, which cannot be either principal, diffuse, or sharp. Unless the spectrum contains more than four types, it is safe to call this the fundamental series. In accordance with the constant frequency shifts explained above, there is also the shifted series $(1S) - (mF)$. Lack of proper observations (which are very

difficult to make presents us from being quite positive about this series, but the course of it so far as it is known, is shown in Table VI. This series is probably analogous to those formerly called SL_3 in Ca and Sr.

COMBINATION SERIES IN THE TRIPLET SYSTEM

Series $(1s) - (mp)$. This combination is strong in Ca and Sr, and its course may be inferred from analogy. In the article by Popow already referred to, one term of the series is given, but in my opinion the identification is incorrect; his arrangement leads to a value of $(1p)$ which is greater than $(1s)$, so that the line $(1s) - (1p)$ should have a negative frequency in Ba. $(1s) - (1p)$ has, of course, a negative frequency, but no series has yet been shown to have two members of this sort, and I am reluctant to admit such a possibility. I have therefore rejected his arrangement.

Since both $1d$ and $1p$ are each triple, the differences $(1d) - (1p)$ give us nine wave numbers. Of these, three do not occur as real lines, and one which probably exists as a faint line, bracketed below, is "covered" by a very strong line of another series which occurs quite close to it. This group is arranged according to the Rydberg scheme in the following manner:

Group $(1d) - (1p)$

				21709.0
				72.4
		21600.9	181.4	21781.4
		171.6		
21429.3	381.0	21771.6		[21953]

The identification of this group leads to the value of $(2p)$ and hence to a triplet of the principal series in the ultra-red, given above, of which the third, and faintest, line has not yet been observed. An effort to find the next member of this series, $(1d) - (3p)$, led to the discovery, in a photograph of the vacuum arc, taken by myself, of a very faint pair of lines, the first near λ 3790.27, apparently the strongest of this group. This observation needs to be supported by observations of the other lines of the group.

Series $(2s) - (mp)$. This series occurs, to the extent of one term only, in the ultra red of Ca. It probably occurs in Ba also.

The strongest line resulting from this combination is the line at [illegible] and Randall has observed a line at [illegible]

COMBINATION SERIES IN THE SECOND SPARK SPECTRUM

Series $(1D)-(mI')$. This series is the one which was found in Ca and Sr and there called SI.[1] It is a shifted series, an exact copy of the principal series, but shifted by a frequency difference of 11305.5 to the new limit which has been identified above as $(1D)$. An objection may be raised to this series as the third line of it is fainter than the lines on either side. An abnormality of the same sort, however, occurs in the principal series, and the objection may not therefore be vital.

TABLE VII

SERIES $(1D)-(mI')$

λ	ν	Term mI'	w	Shift Observed
15090.4	6624.9	17930.3	8	11305.3
4520.46	22118.2	6812.5	5	11305.7
4004.98	24974.2	5670.6	5	11303.6
3688.45	27104.5	4799.0	8	11305.0

Series $(1S)-(mI')$. This series is suggested tentatively, but as the three lines in the table give very accurate shift numbers I am disposed to regard it as real.

TABLE VIII

SERIES $(1S)-(mI')$

λ	ν	Term mI'	Shift Observed	w
3501.12	28554.3	17248.8	11305.4	8
2785.36	35893.9	6588.4	11305.5	2
2646.50	37774.8	4469.6	11305.2	3

Series $(2S)-(mP)$. This series ought, by analogy with other elements, to occur in Ba. Two members are observed, fairly near their calculated places. The first, and supposedly strongest, member should lie in the ultra-red, and has not been observed; if this line is not found, the existence of the series will become somewhat precarious; but it must be said that all series involving

[1] *Astrophysical Journal*, 32, 156, 1910

the terms mF' show an anomalous lack of intensity for $m = 2$ or 3, and this one series have the same peculiarity.

TABLE IX

Series $(1S)$ $-(mP)$

		m	Terms (mP)	Shift Number
		2	[30485]	.....
		3	30301	25629.0*
		4	15728	25627.7

* The calculated value of the shift number is 25629.0, which is 25629.0

Series $(1F')$ $-(mF')$. This is probably a very faint series. Only one line has been observed, which is $(1F') - (4F')$; calculated ν 13494.1, observed ν 13494.6 (λ 7527.6). Meggers reports this line as absent from his plates, but an inspection of the plate under the most favorable lighting, for which I was generously given an opportunity, showed the line as present, though faint. The next line of this series should be at ν 17845, but has not been found.

Series $1S$ $-mS$. This combination is possible. It gives us ν 25629.0, and there is a faint line observed at λ 3900.37, (ν 25631.5). The agreement is only fair.

OTHER SYSTEM COMBINATION SERIES

Series $1S$ $-mp_3$. This series in the spectra of other elements has recently come into considerable prominence. It is strongly enhanced in the low temperature oven spectra, and occurs in Ca and Sr. Some recent plates taken by Dr. King show that the only line in Ba which has this property and lies in the proper part of the spectrum for the line $(1S) - (1p_3)$ is at λ 7911. The proper region can be found by getting $(1S)$ approximately from the principal series of single lines by calculation, and then subtracting from it the better known value of $(1p_3)$. In this way the line $(1S) - (1p_3)$ is identified, and from its wave-number and the quantity $(1p_3)$ the value of $(1S)$ is redetermined with greater precision. This series fades away sharply in this group of elements. The second line should be a faint line and its calculated position is λ 3244.20. King's plates show an iron line at 3244.18, and it has not been possible to resolve these two, or to get an

absolutely iron-free spectrum. One of his plates, in which Ba is very rich and Fe faint, shows this line relatively strong, compared with other Fe lines, and its position when measured came out exactly at 4244.20. As the dispersion on this plate is 4.56 A per mm, the error of measurement is considerably less than 0.01 A, so that this line is undoubtedly present. The next line of the series has not been found, on account of faintness.

Series $(sd_2) - (mP'_1)$. This combination series is fairly strong. Like all the other series involving the terms mP', this series is somewhat abnormal in the intensities of its lines, the second line being faint. The two closely related series $(sd_1) - (mP'_1)$ and $(sd_2) - (mP'_2)$ might be expected to occur. There are two lines which might possibly be members of the series $(sd_1) - (mP'_2)$, but the agreement is not very good, and there is no other evidence in favor of the existence of these combinations.

TABLE X.

SERIES $(sd_2) - (mP'_1)$.

λ	ν	Terms mP'	m	Shift Separation
11304.39	8844.1	5397.0	4	9246.4*
4284.99	23331.2	9484.1	5	9246.0
3599.49	27774.9	5074.2	6	9245.8
3414.84	29284.3	3565.8	7	9245.2

* The calculated shift number is $\nu(sd_2 - sd_1) = 9245.7$.

SUMMARY

The spectrum of barium contains three systems of series, the triplets, the single lines, and the pairs. The first two systems are here shown to contain at least four types of series each, together with various combination series. In the triplet system the four type series are not new, but are here extended and revised; two combination series in this system are suggested. In the single-line system, the principal series is revised, and the other three type series in this system are shown in all probability to be present; several combination series in this system occur, including the series formerly called SL_2 and SL_3; and two inter-system combination series are also found.

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REVISION OF THE SERIES IN THE SPECTRUM OF CALCIUM

By F. A. SAUNDERS

ABSTRACT

Series in the spectrum of calcium.—A study of the triplet and singlet systems, based on recent observations including some with *new lines*, has led to the extension of most of the series, the calculation of the limits with greater precision and the identification of various combination series. The diffuse series of triplets is extended to 15 terms and is shown to exhibit numerous anomalies. Altogether, four triple series of each system and eight probable combination series are given and also indications of three possible inter-system combination series.

In the course of a study of the series in the spectrum of Ca some new data have been obtained which it now seems worth while to summarize in a brief article. A knowledge of the structure of this spectrum is much to be desired. While it is relatively simple, it is less so than He or Na and those features which are new may guide us toward the solution of still more complex spectra. It has not yet been possible to classify all the lines in the Ca spectrum, but a considerable advance in this direction has been made. More observations are needed, especially in the infra-red, where the experimental difficulties are formidable.

The sources used in this work have been the vacuum lamp,[1] the vacuum arc, the hot quartz vacuum tube, or oven, besides all

[1] *Astrophysical Journal*, **44**, 321, 1916.

the more usual ones. Observations have been kindly furnished by Dr A S King from plates taken with his vacuum arc, and Professor H M Randall has contributed valuable as yet unpublished observations in the infra red region. Certain facts in regard to the Zeeman effect for Ca the writer owes to Professor Paschen and his collaborators. The most valuable among the recent published sources of information about the Ca spectrum has been the work of Crew and McCauley,[1] which covers the vacuum arc spectrum very thoroughly within a certain range, and with admirable precision. Their wave lengths, on the international system, have been taken as a basis for all the lists here given, though mention should also be made of the work of Holtz[2] done, unfortunately, on the arc in air, where the diffuseness of some of the lines prevents accurate measurements. Lorenser's dissertation[3] furnishes observations in the red, and a partially successful attempt at a classification of some of the lines into series.

The spectrum of Ca consists of three systems of series, each containing at least four types of series, together with combination series derived from these. Attention is here limited to two of these systems, the triplets and the single lines or singlets. Inter system series, obtained by combinations between these two, are known, but no such combinations involving the third system, that of pairs, have been found. This is one of many facts that lead to the belief that the pair system is given by a different vibrating mechanism, presumably ionized Ca, or Ca$^+$.

The four type series in each system are called the principal, sharp, diffuse, and fundamental series. The notation used has already been explained.[4] The symbol (mp), for instance, stands for one of the "terms" (wave-number differences between limit and individual line)[5] of the principal series of triplets, m having any integral value from unity up; the corresponding symbol (mP) refers to the principal series of singlets. The numeration adopted

[1] *Astrophysical Journal*, **39**, 101, 1914.

[2] *Zeitschrift für wissenschaftliche Photographie*, **13**, 101, 1913.

[3] Tübingen, 1913; review, *Astrophysical Journal*, **41**, 155, 1915.

[4] *Astrophysical Journal*, **41**, 155, 1915.

[5] In the language of the Bohr theory, each term is proportional to the energy of the radiating electron in one "stationary state."

for m varies somewhat among different writers. Paschen uses 1, 2, 3, etc., for the values of m in the terms (mS), while Fowler and others prefer whole numbers. Theory furnishes as yet no safe guide in this matter. The lowest value of m in (mp) is taken as 2 by Paschen and as 3 by Fowler, and in what follows. For the diffuse series Paschen begins with 3, Fowler with 2, while I have preferred 3 for the convenience of having m always the same as the number of the corresponding series member, counting from the beginning of the series.

The results are presented under the headings of the individual series, classified under the triplet system, the singlet system, and inter system combinations.

THE TRIPLET SYSTEM

Principal series of triplets $(1s) - (mp)$. The first member of this series is also the first member of the sharp series; its lines are AA 6162.18, 6122.22, 6103.72. The corresponding terms are 43988.7, 44094.6, 44146.9. The next triplet in this series has not yet been satisfactorily observed, but its position can be fixed through the combination $(2d) - (2p)$ given below. The predicted wave lengths are 10982.7, 10942.2, 10950.7; two lines have been observed at 10980.3 and 10935.2; the third line is the faintest of the three and has not yet been found. This triplet is entangled with the first member of the diffuse triplets, and has not yet been satisfactorily resolved. The third triplet of the series has not been observed; it must be very faint, as a two-hour exposure of the vapor lamp spectrum with a large prism spectrograph, using a dicyanin stained plate, gave no trace of it. Its position can be calculated, however, from the combination $(2d) - (4p)$ given below, and the calculated wave-lengths are 9108.71, 9105.40, 9098.95; of these the last is the strongest. The fourth member of this series cannot be calculated with certainty, as the combination $(2d) - (4p)$ has not been identified satisfactorily, but there are indications pointing to a value 4342.7 for the term $(4p)$, the three values of which would be very close. If this is correct the triplet would be near λ 7448.2, but it has not been found.

merely on account of its relationship with the sharp series which is that characteristic of principal series in the spectra of other elements, such as Na. It is to be noted that Bäcklin selected a value for σ_2 or in his notation σ_3 which is different from the one here given. His choice cannot hold for reasons which I have recently pointed out[1] in the analogous case of Ba. The term to which he calls attention must belong to a still unknown series.

Sharp series of triplets $(2p - ms)$. The accompanying tables give the wave lengths of the lines of this series in international units, together with the wave number differences within each triplet, which should remain constant, and the "terms." In con-

TABLE I

SHARP SERIES OF TRIPLETS $(2p - ms)$. LIMIT 15388 ± 14 AT 14345° ±

λ I A	Δν	λ I A	Δν	λ I A	Limit	m
6162 18	105 9	6122 59	53 5	6102 13	15765 2	1
3973 52	105 9	3951 05	53 5	3928 00	8810 5	2
3487 61	106 0	3464 55	53 4	3442 48	5353 5	3
3286 06	105 8	3264 66	53 4	3243 09	3355 6	4
3180 52	105 8	3160 85	53 4	3139 41	2356 1	5
3117 66	105 9	3097 59	53 3	3076 30	1757 4	6
3076 99	105 7	3057 01	53 5	3036 05	1358 6	7
3049 01	105 8	3029 22	53 8	3008 54	1080 1	8
3028 97	104 9	3009 37			881 5	9
3014 01					742 3	10

nection with this table it should be noted that the line λ 3076 99 was measured by Crew and McCauley, and that the lines λλ 3049 01 3039 21, 3028 97, 3019 37, and 3014 01 are new. The line 3034 52 is most probably a diffuse series line, which nearly coincides with the fainter sharp series line to be expected in this neighborhood.

This series was one of those first found in Ca. It is of medium strength, but its outer members fade rapidly and become diffuse

[1] *Annalen der Physik*, **45**, 160, 1914.

[2] *Astrophysical Journal*, **51**, 15, 1920.

in an [illegible] A long column of luminous vapor at a low pressure is required to give the new lines.

Diffuse series of triplets (1p) – (md). This is the most obvious series in the Ca spectrum. Its lines are given in Table III. It should be noted that the lines λλ 3109, 3108, 3090, 3080, 3071.58, [illegible] and 3018 were measured by Crew and McCauley but are here classified for the first time. The lines

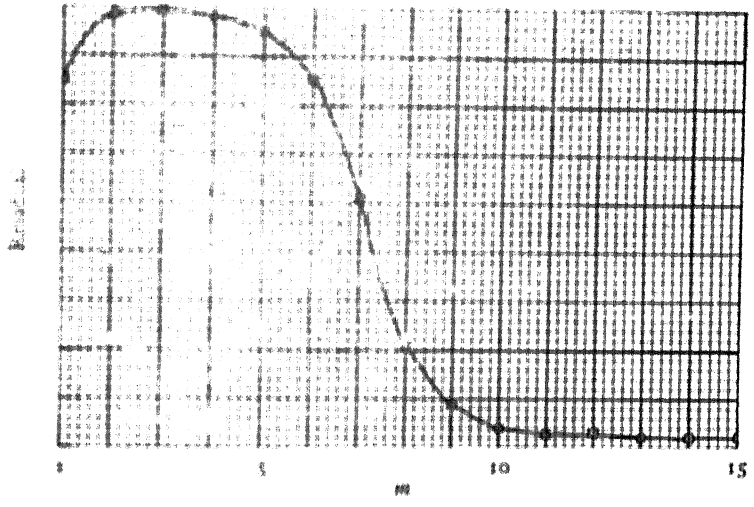


FIG. 1. Curve of Residuals for Ca (1*p*) – (*md*)

λλ 3095, 3081, 3071.97, 3067, 3055.55, 3020, 3006, 2996, 2988, and 2982 are new.

This series exhibits a remarkable type of irregularity, similar to that already found in the narrow triplets of Ba, and quite unsuspected from previous observations. The usual diffuse triplet really consists of six lines, the first three being quite close, and forming the first and strongest "line" of the triplet; the middle line on closer inspection proves to be a close pair. The narrow triplet formed by the first three behaves like a principal series in itself. Not only does it shrink to a single line in passing out toward the limit of the series, but its intensities are arranged in the manner

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
1256 11 1255 88	105 5	[illegible]	[illegible]	[illegible]	[illegible]	5
1151 98 1150 75	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	6
1109 51 1108 58	105 4	[illegible]	[illegible]	[illegible]	[illegible]	7
[illegible] 1080 82	105 4	[illegible]	[illegible]	[illegible]	[illegible]	8
1055 55 1055 12	105 1	[illegible]	[illegible]	[illegible]	[illegible]	9
1034 31	104 4	[illegible]	[illegible]	[illegible]	[illegible]	
1018 55			[illegible]	[illegible]	[illegible]	10
1000 22	105 9	[illegible]			[illegible]	11
1996 67					[illegible]	12
1988 98					[illegible]	13
1981 89					[illegible]	14
					[illegible]	15

of principal series. It is also connected with another series, the fundamental, in precisely the same way that the principal is connected with the sharp (the Rydberg-Schuster law). The shrinking of these little triplets is in most cases progressive and regular. I have recently made a special examination of the corresponding triplets of Zn and of Cd and found no irregularity, even though the exposure series which was used revealed a large number of new series members. But in the case of this series in Ca, the shrinking is checked at the fourth member, and the group then widens progressively in the three following members, subsequently shrinking rapidly. All this happens without disturbing the constancy of the differences of wave number, as is shown in the tables. The "curve of residuals" also is far from simple, as shown in Figure 1, though it is smooth, indicating that the observed perturbations are real; this means that no simple formula can be made to fit the series. Another anomaly is furnished by the intensities; the eighth triplet is unduly faint, or the few following unduly strong.

Fundamental series of triplets (*nd*) – (*mf*). This series has been considerably extended, and its limit is here given with much greater precision than before. Its terms are really complex, prob-

TABLE III

Fundamental Series of Triplets (*nd*) – (*mf*). Limits 28911.6, 28955.1; 28968.8

λ I A	Δν	λ I A	Δν	λ I A	Terms	m
4585.93	22.1	4585.48	22.6	4582.57	7183.9	1
4585.71						
4509.33	22.2	4509.04	22.2	4509.05	4541.5	2
4527.53	22.2	4527.25	22.3	4527.27	4139.5	3
4513.32	22.2	4513.05	22.3	4513.07	3998.1	4
4506.78	22.2	4506.51	22.3	4506.53	3754.1	5
4503.18	22.2	4502.91	22.3	4502.93	3583.3	6
4501.08	22.2	4500.81	22.3	4500.84	3417.7	7
4499.74	22.2	4499.47	22.3	4499.49	3293	8
4498.85	22.2	4498.58	22.3	4498.61	3174	9
4498.23	22.2	4497.96	22.3	4497.98	3060	10
4497.77						

ably triple, but the lines are too close for measurement in all but one case, resolved by Janicki. From λ 4038 on, all the lines in the table of this series are new.

Series $(2d)\ -(mf)$. If we subtract the three terms $(2d)$ which are 12749.4, 12740.5, and 12736.4, from the three terms (mf) given above we obtain nine real lines of which six are real lines in a narrow group in the orange and are completely observed by Lorenser. This is the second member of this series, the first being the first of the diffuse triplets, taken with negative sign. Since the principal series lines converge to a single limit the present series, which begins as a complex group should converge to a narrow triplet. The third member of the series is faint, but comes out well in the vapor lamp spectrum and in the vacuum arc. Its lines, with one exception, are in the list of Crew and McCauley. They are λλ 4812.28, 4807.86, 4803.43, 4801.00, 4800.62, 4797.42, arranged in the order of their group positions. The fourth member must be extremely faint. Lines at λλ 4676.44 and 4672.49 seem to belong to it, but it was impossible to complete the group.

Series $(2d)\ -(mf)$. This series lies in the ultra red and was given by Paschen. Only one member has been observed, a close triplet at λλ 22055.9, 22024.6, and 22010.0 $(m=2)$. Randall (unpublished) has found tentative indications of a second member near λ 14378.

Series $(2p)\ -(md)$. This is a possible but still doubtful series in the ultra-red. It probably takes the form of groups of six lines. Three, at λλ 16200.0, 16163.2, and 16144.8, have been observed, which seem to form part of such a group, but it is not fully resolved. The next member has not been found.

THE SINGLET SYSTEM

Principal series of singlets: $(1S)\ -(mP)$. This series is the one formerly called *SL1* and it has been known for some time.[1] It contains the flame line λ 4227, and most of its lines are of the same character, that is, easily reversed. There is an anomaly in the intensities, however; the second line is much too faint, and does not reverse. A similar peculiarity appears in the corresponding series in Sr and in Ba. The weak line must belong to this series, as its "term" leads to combinations which exist. The "curve of

[1] *Physical Review*, 1, 332, 1913

residuals" for this series has a point of inflexion, as Lorenser pointed out. The terms given in the table for this series are averages obtained from this series and the series $(1D)-(mP)$ given below.

Sharp series of singlets $(1P)-(mS)$. This series must, by analogy, be a fairly strong one, but it is difficult to settle its course with certainty. The information furnished by the Zeeman effect fails to separate this from any other series of singlets, and observations are lacking in the infra red, where particularly needed. There are no constant differences to guide our choice of lines. Lorenser

TABLE IV

System of Singlet Series

m	Fundamental $(1P)-(mS)$		Sharp $(1P)-(mS)$		Diffuse $(1P)-(mD)$		Fundamental $(1D)-(mP)$	
	λ I.A.	Terms	λ I.A.	Terms	λ I.A.	Terms	λ I.A.	Terms
1	4326 73	23103 4	4326 73	40404 8	(5 55μ)	27455 3	4878.13	6061.3
2	2202 65	45373 1	10548 .0	25988 .2	7340.10	13666 .3	4355.10	4500.0
3	1393 58	71773 9	5512 .98	17518 .4	5188.85	6385 .5	4108.55	3122.6
4	1075 49	93131 4	4847 .09	13028 .0	4085.36	4314 .7	3972.58	2289.7
5	0900 38	107959 6	4496 .16	11417 .3	4412 .30	2904 .7	3889.14	1749.8
6	0810 28	118874 6	4312 .31	10469 .4			3833.96	1379.8
7	0748 68	127623 3	4193 .22	9807 .7			3795.62	1116.3
8	0697 49	134638 .1	4112 .64	9461 .5			3767.42	919.3
9	0683 73	139505 9	4084 .5	9176 .0				
10	0671 64	143174 6						
11	0664 55	145888 5						

sketched out an arrangement for the beginning of this series in the expectation that later observations would yield lines to complete the series as outlined. Such lines do not, however, appear, and instead we have others which fail to fit into his scheme.

The first term of the series must be the limit of the principal series; the limit of the series is likewise known. Hence the second term may be calculated, roughly, by one of the series formulae. Any one of two or three lines in the infra-red might serve as the corresponding line, the second of the series; the one here chosen works out best, and the rest of the series follows with reasonable certainty. Two of the lines run parallel to two ultra-violet lines, which must belong to the combination series $(1S)-(mS)$ given

below. This greatly strengthens the foundation on which the arrangement rests. The curve of residuals is not a simple one, but is simpler than that given by any other grouping of the available lines. The Zeeman effect for these lines, so far as known, is correct, namely, normal triplets. The last half of the lines in the table are new, having been obtained from vacuum sources. The last one is very doubtful.

Diffuse series of singlets: 21′ — m1′. The limit of this series is, of course, known, being the term 21′ of the principal series. In spite of this fact its course would be difficult to discover were it not for the existence of a parallel series in the ultra violet having the same terms. The last three lines are thus classified as belonging together, though the series to which they belong is not identified in this way. The line here given at the head of the series has not yet been observed, and involves a negative frequency. Analogy with Ba points to its existence, and the negative frequency offers no special difficulty, if one is willing to admit the possibility of such a thing in other series. For instance, the first member of the principal series of most elements is also a member, but with negative frequency, of the sharp series. Something similar occurs with the diffuse triplets of Ba, and the diffuse pairs of Ca, Sr, and Ba. It is evidently common with diffuse series.

The limit of the two series formerly known as *SI.*2 and *SI.*3 is 1, λ = 2745. This number must, according to the combination principle of Ritz, itself be a term belonging to some series in the Ca spectrum. There is no series but this one to which this term can belong without producing a quite unreasonable sequence of terms. This must be the term (1*D*), the first term of the diffuse series, and the limit of the fundamental. An analogous conclusion may be drawn for Sr, and has already been given for Ba. The identification of this series as the diffuse is further strengthened by the fact that Takamine[1] has observed that λ 4685, one of the lines of this series, is affected by an electric field; and it seems to be true that the Stark effect is greater for diffuse series than for any others. The identification of the series *SI.*3 as the fundamental follows from the choice of the term (1*D*) above, and appears also to be reasonable,

[1] *Kyoto University Memoirs*, 3, 173, 1918.

since its terms in common with those of other fundamental series, have values not far from those of the hydrogen series.

Lorenser has outlined the beginning of this series, but, as in the case of the preceding, incorrectly. He began it with a negative-frequency line, as I have done, but a different one, and one which leads to no combinations, and has apparently no justification. He also included a line λ 6362, which certainly has the wrong Zeeman effect. Two of his lines, λλ 5189 and 4685, are, however, included in my list.

Fundamental series of singlets: $(1D)-(mF)$. The foregoing argument leads to the identification of this series, formerly known as *SL3*. Its lines are here given with greater precision, and the last three are new. The limit is much more accurately determined than before. The similarity of the terms of this series and those of the fundamental series of triplets makes it possible to obtain a useful check on the values of the limits of both series, furnishing a direct connection between the triplet and singlet system, in addition to that given by inter-system combinations. The limits of all the series given in this paper have been adjusted to the best values consistent with these relations.

COMBINATION SERIES IN THE SINGLET SYSTEM

Series $(1D)-(mP)$. This is the series formerly called *SL2*. Its wave lengths are as follows: λλ 6717.69, 5041.61, 4526.94, 4240.46, 4058.91, 3946.05, and 3871.54, of which several are now more accurately known, and the last is new. The series is of medium strength in vacuum sources, but faint and diffuse in air. The first line of this series is probably at 5.55μ, and is the first line of the diffuse series also. It has not yet been observed.

Series $(1S)-(mD)$. The wave-lengths of this series run: λλ 4575.43, 2680.36, 2329.33, and 2221.91, as far as they have been observed. It is a faint series. The second line coincides almost exactly with a line of the principal series of Na, which is nearly always present as an impurity. I have inferred the presence of the Ca line only from the fact that the line was slightly stronger than one would expect; the identification is therefore somewhat

doubtful. The last two lines were found only on plates taken with the arc in air, and their diffuseness prevents accurate measurement. A photograph reproduced in this *Journal* shows some of them.

Series $(1S)-(mS)$. This series is similar in character to the preceding. Its first line $m=2$ should appear very near to the strong line λ 3888.87, but could not be observed, probably on account of the spreading of its strong neighbor. The next three lines are at λλ 2302.22, 2254.40, and 2237.58.

Series $(1P)-(mP)$. This combination is common in other spectra. Here it is very faint and somewhat doubtful. The first line appears to be λ 7644.25, observed by Lorentser. The second line should appear near λ 4540, in a region usually "occupied" by a band. The third line was found in its predicted position at λ 4020.25, in vacuum sources.

Series $(2S)-(mP)$. For $m=2$, the calculated value of ν is 3415; Randall has observed a line at 3412. For $m=3$, the calculated value of ν is 8362, the observed 8360. For $m=4$ no line has been found. The series is still doubtful.

Series $(1D)-(mS)$. For $m=3$, the calculated value of ν is 10936.9, and there is a line at 10934.2, observed as a faint and very diffuse line in the arc in air. The next line is not found.

INTER-SYSTEM COMBINATION SERIES.

Series $(1S)-(mp_1)$. The first line of this series appears in the vacuum oven as quite a strong line, it occurs at λ 6572.78, and was identified by Paschen. The next line is very faint, but was observed at λ 2734.82, calculated λ 2734.84. The third line could not be found.

Series $(1p_1)-(mS)$. This series may exist. Its first line has not yet been found, but the second occurs as a faint line at precisely the predicted place, λ 3761.72. The combination $(1p_1)-(4S)$ also occurs, but this is probably merely a numerical coincidence.

Series $(1D)-(mp)$. This series is very doubtful, but is included because the combinations $(1D)-(2p_1)$, $(1D)-(2p_2)$, and $(1D)-(3p_2)$ lead approximately to faint and diffuse lines in the arc in air. The coincidences may be accidental.

[1] *Astrophysical Journal*, 43, 138, 1916.

SUMMARY

The spectrum of Ca consists of three systems of series. Each system contains four type series and combinations formed from these. The triplet and singlet systems are here studied, on the basis of new observations mainly from vacuum sources. In the triplet system, the type series are given, several new lines being added, and the limits calculated with considerable precision. The diffuse series of triplets is shown to exhibit certain curious anomalies. Three combination series in this system are probable. In the singlet system also the four type series are given, and five combination series suggested. There are also indications of three series formed by combinations between the triplet and singlet systems.

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A REVIEW OF THE SERIES IN THE SPECTRA OF THE ELEMENTS.

BY

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The analysis of the spectra of the elements into series and systems of series, and the study of the relations among these within the spectrum of one element, and among different elements, is a subject which has received but little attention in spite of its obvious interest. For thirty years or more it has been known that the vibrations of the atom are not haphazard, but are often arranged on a regular order, suggesting a series of overtones in acoustics. In certain cases, such as hydrogen, or zinc, this arrangement is quite conspicuous, and was recognized as soon as the full spectrum was obtained, in others, the spectra are so complex that there is little reason to hope that we may ever work out their structure.

The interest in the problem lies in the information which these studies may yield as to the nature of the atom and the physical processes going on within and about it, and in these days no information about the atom can be branded as useless. The difficulties which present an immediate solution are very numerous. The eye is sensitive to but a small part of the spectrum. For the investigations in question, the entire spectrum must be studied, from the shortest ultra violet waves to the longest ultra-red, and several different experimental methods and much elaborate apparatus have to be employed in order to yield such a wide sweep of spectrum. Moreover, we do not possess means of agitating the atom which are sufficiently vigorous to make it

give its "complete" spectrum, a term which will always have a very vague meaning. Some lights are richer in lines than others, but, at the best, even with a vast [illegible] we have to be content with a very imperfect view of the lines we wish to survey.

Certain comparatively recent discoveries have been a great assistance when applied to this problem. If the source of light is placed in a strong magnetic field each line of the spectrum breaks up into a little group of lines (Zeeman effect), the arrangement of which appears to be characteristic of the series to which the line belongs. Something similar happens, at least in certain cases, with electric fields (Stark effect). But these effects cannot be observed for faint lines, and, since practically the majority of the lines in all spectra seem to be faint,

The present state of the experimental study of spectrum series is one of flux, and whatever may be written about it now will probably be hopelessly out of date in half a dozen years. Something of the same sort may be said for the theoretical side of the question. Bohr, Sommerfeld, and others have built up a model of a simple atom whose unconventional actions would have shocked physicists of twenty years ago, but which seem to be capable of yielding the observed spectra. At the present writing, this very remarkable success has been obtained only for the simplest type of atoms, containing merely the nucleus and one electron. This limits it to the spectrum of hydrogen and the spectrum of ionized helium. Other spectra, such as that of ordinary helium, are being attacked, but it is too early to say with what success.

The present article will not include any account of the theoretical investigations. These have been treated by Sommerfeld in a book, and are being made accessible to English readers in other ways. No comprehensive account of the experimental side of the problem exists. The beginnings of it may be found in Kayser's monumental "Handbook of Spectroscopy," but that book is now quite out of date on this branch of the subject. A book is to be published shortly by Professor A. Fowler, of London, which will give us an authoritative summary by one who has contributed largely to its development. In anticipation of this work, however, a brief attempt will be made in this article to outline our present knowledge of spectrum series. The matter

will be given [illegible] in the order of the simplicity of their [illegible] which is nearly the same as the historical order in which [illegible] series will be found [illegible] that occur.

[illegible] the spectra of hydrogen, the simple, [illegible] spectrum, recently shown [illegible] the hydrogen molecule. The simple [illegible] series, occurring in at least three [illegible] the spectrum, as though transplanted unchanged. The [illegible] differences are what remain unchanged in [illegible] series are called parallel series. Any series consists of [illegible] arrangement of lines whose spacing diminishes regularly [illegible] a limit whose frequency is finite, and is sometimes called the "convergence frequency" of the series. The intensities of the lines fade away the nearer the limit is approached, and usually it happens that only very few of the lines can be observed. In [illegible] sources it is rare that more than 12 lines of a series can be observed, the maximum number is about [illegible] H. W. Wood from the absorption of [illegible] vapor.

It is usual to speak, not of wave lengths, but of their reciprocals called wave-numbers, these being the number of waves per cm. and it will be convenient to define the "term" of a series line as the difference of wave-number between the limit of the series and the individual line. Thus the hydrogen series yields a sequence of terms which remain unchanged in each repetition of the series though the limits in the three cases are very different.

The visible portion of the spectrum consists of four lines of the "Balmer" series, the rest of which is in the ultra-violet. This series can be represented by the formula

$$\nu = N\left(\frac{1}{2^2} - \frac{1}{m^2}\right)$$

where N is the so-called "universal series constant," having a value near [illegible], and m takes in succession the integral values 3, 4, 5, etc. This formula yields the observed wave-numbers to quite an extraordinary degree of accuracy, though if the utmost refinement be demanded there should be a correction term, of a nature [illegible] the m. The lines are, moreover, actually very close doublets whose frequency differences are now known to remain approximately constant throughout the series.

In the extreme ultra-violet region the series

$$\frac{1}{\lambda} = N\left(\frac{1}{1^2} - \frac{1}{n^2}\right)$$

occurs, discovered by Lyman and beginning with the line $\lambda 1216$. Paschen has found three lines in the ultra red which belong to the series

$$\frac{1}{\lambda} = N\left(\frac{1}{3^2} - \frac{1}{n^2}\right)$$

Other series may exist in the deeper ultra red, but these are very faint. The whole set of series, and therefore the whole spectrum of atomic hydrogen, can be represented by the formula

$$\frac{1}{\lambda} = N\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

where, in general, the lines are stronger the smaller are the integers n and m. The smallest value for n is 1, and for m is always the integer next larger than n. The Bohr theory has had its greatest success in the explanation of this spectrum.

The Sodium Family.—The elements of this family yield spectra which are closely similar to one another, and are one step less simple than that of hydrogen. Each consists of four chief series, and each line in each series is double. The four series are known as principal, diffuse or first subordinate, sharp or second subordinate, and fundamental. The latter are called the "Bergmann" series by German writers, though improperly, as Fowler was the first to find one of this type, and Runge the first to point out their true relationships. These four type series have certain characteristics which are worth noting. The *principal* series contain the chief line of the spectrum (the D line in the case of Na), which is produced in flames, and readily reversed in hotter sources, due to self-absorption. The separation of the pairs is not constant in this series, but they shrink rapidly in passing out toward the limit. The lines of a principal series pair have slightly unequal intensities, the stronger one being on the side of the shorter wave-length. The *diffuse* and *sharp* series have constant wave-number differences in each pair, and equal to that for the first pair of the principal series; their lines have an aspect well indicated by their names; and these two series converge to a common limit. The stronger line in each pair is here the one of *longer* wave-length. They require higher temperatures

of more vigorous excitation for their production than does the principal series. The *fundamental* series is a faint series of narrow pairs, lying in these cases in the ultra-red; its name is somewhat misleading.

Any of these series may be represented approximately by a series formula, of which there are several types. The general type is

$$\nu = \frac{N}{[n + a + f(n)]^2} - \frac{N}{[m + b + f(m)]^2}$$

where N is the universal series constant, as before, though there are indications that its value should change slightly; n and m are variable integers, n having a single value for the whole of a series, while m takes a set of integral values in succession; a and b are constants, and the functions $f(n)$ and $f(m)$ may take many forms, none of them quite satisfactory. Fair success is obtained by giving the functions the form c/n^2 and d/m^2, c and d being new constants, but in many cases no simple form can possibly serve for these functions. The portion of the denominator written as $a + f(n)$ is sometimes referred to for brevity as the "residual"; it should settle down to a constant value as we proceed toward the limit of the series, and usually does so with rapidity. These formulæ have as yet no very sound theoretical basis, nor any established and universal shape; hence it has proved convenient to dodge the question of how they should be written by using abbreviations. In the above general formula the right-hand half of the expression for the wave-number is what we have already called the term, and we indicate it by the symbol (m,b), no matter how complex the formula actually used might be. The letter bracketed with m in this symbol is usually chosen to indicate the series to which it refers; thus, the letters *p,s,d* and *f* refer respectively to the principal, sharp, diffuse and fundamental series; for example, (1,p) stands for the first term of the principal series, (3,s) for the third term of the sharp. In the case of such elements as have series of other sorts beside pairs, the letters indicate the sort; thus in such elements, for example in Ca, small letters are used for series of triplets, large letters for single-line ("singlet") series, and Greek letters for pair series, except that German authors have so far used old Gothic letters instead of Greek. These distinctions are, naturally, not to be made, and have

no meaning in the case of the elements of the sodium family, where all series are pairs.

The variable integer m has its lowest value for the first line of the series. In no cases but those of hydrogen and ionized helium can this integer be definitely settled as yet; in fact, since m is always associated with an added constant whose value is anything we please, the value of m becomes equally adjustable. German writers use for the first line of the series the value $m = 2$ in the case of the principal series, 3 for the diffuse and 4 for the fundamental, while for the sharp they use values intermediate between integers, namely 1.5, 2.5, 3.5, etc. Some English-speaking writers prefer to put $m = 1$ for all first lines; such theoretical indications as there are rather favor the German custom.

A principal series may be written, in the symbolic way explained above, $1/\lambda = (1,s) - (m,p)$. The limit of the series is the term (1,s), which is the first term of the sharp series, as the letter indicates. This connection between the principal and sharp series amounts to saying that they have a first member in common. On this idea, the first line of the principal series has the wave-number (1,s)−(1,p), while the first line of the sharp series is (1,p)−(1,s). The latter is negative, and it might well be objected that a negative wave-number is meaningless. The Bohr theory offers a possible explanation of this curious case, and others of the same sort, as indicated below. The *Rydberg-Schuster law* says that the wave-number difference between the limit of the principal series and the limit of the sharp and the diffuse series (which they share in common) is equal to the wave-number of the first line of the principal series. If this is otherwise expressed it amounts to saying that the limit of the sharp series is the first term of the principal. This fact was used above in writing the first line of the sharp series as (1,p)−(1,s). The whole of this series would be indicated by $1/\lambda = (1,p) - (m,s)$.

The diffuse series is given by the formula $1/\lambda = (1,p) - (m,d)$. The terms (m,d) and (m,p) are each double in the case of pair series, and in reality the diffuse pair contains three lines, the first and stronger line having a faint satellite. This is noticeable only in the case of wide pairs (*e.g.*, Rb and Cs), and even then only in the first few series members, for the reason that the satellite and the major line close up together.

The fundamental series is given by $1/\lambda = (1,d) - (m,f)$. Its

limit is the first term of the diffuse series, a law due to Runge. The terms (m,f) are also double, though very close in most cases. Since the two values of (1,d) are not far apart, this series consists of narrow pairs, of which each line is itself a close double. While this complexity has been found only for Cs, there is every reason to believe that it is general. We are dealing here with what is generally called the "fine structure" of the lines, and a great many series lines prove to be complex when examined under the highest resolving powers. In most cases this complexity is so difficult to observe that we may safely ignore it.

Ritz formulated a so-called "combination law" to the effect that any two terms, chosen from among the lists of those in the four type-series, might be combined, and their difference would give a wave-number which might correspond to a real line. Combinations which occur more or less commonly are as follows: (1,p) − (m,p); (2,s) − (m,p); (2,p) − (m,d); (2,p) − (m,s); (2,d) − (m,f); etc. Of these the first, but only the first, are similar to difference tones in acoustics. In such elements as have systems of triplet and singlet series (*e.g.*, Zn, Ca, etc.), there also occur intersystem combinations, of which the most important is (1,S) − (m,p_2). Here the (m,p) terms are triple, but the combination occurs only with the middle value, indicated by the subscript.

On the basis of the modern theory, the Ritz combination principle can be given a simple physical interpretation. If the outer electrons in the atom can exist in a number of different stationary states, in each of which their energy has a definite value, then the radiation is supposed to occur on the transfer of an electron from one of these states to another. The change of energy which is involved in this event is proportional to the frequency of the light, and the light is supposed to be emitted during this process and at no other time. Thus, the "terms" should be proportional to the energy in the corresponding states, and their differences, which by the combination principle give the frequency of observed spectrum lines, are proportional to the changes in energy associated with the transfer of an electron from one state to another. On this theory, if a negative wave-number occurs, it indicates merely that the electron passes from one state to the other in a direction opposite to that which we might expect on spectroscopic grounds, and this idea involves no special difficulty.

The entire spectrum of Li,Na,K,Rb or Cs could then be written as $1/\lambda = (1,s) - (m,p)$; $1/\lambda = (1,p) - (m,s)$; $1/\lambda = (1,p) - (m,d)$;

(A—(1,d) (m.t.), together with combinations formed from these terms. Most of the combinations which one might test are in the ultra red and are not observed. All combination lines are likely to be faint. Exactly the same combinations have not been observed in all these spectra, but it seems hardly worth while to give the details in the separate cases.

In comparing the spectra of the elements in this group it is interesting to note that the widths of the pairs is proportional approximately, though not exactly, to the square root of the atomic number of the element. It might also be remarked that the spectrum as a whole shifts toward the shorter vibrations with increasing atomic weight, as one might expect from mechanical considerations. These laws appear to be general.

All these elements probably possess another spectrum as yet practically unknown. Traces of it have been found in the heavier elements. This has been called the spark, or enhanced spectrum, but it might better be called the spectrum of the ionized element. It is particularly easy with the elements of this family to detach one electron from the atom. The new spectrum would appear when *two* electrons were detached temporarily, and one of these returned, thus giving us the optical vibrations of the atom minus one electron. As the atom in this condition would probably have a structure resembling the inert element to the left in Mendelejeff's table, *i.e.*, to Neon, Argon, etc., it is not surprising that it is difficult to tear off a second electron, and obtain the spectrum in question. It is probable that the "Grundspektra" of Goldstein are mixtures of this spectrum with the ordinary one.

The Calcium-Zinc Family.—Passing to the next column of Mendelejeff's table of the elements, we find more complicated spectra, which are not as yet quite completely understood. Each contains at least four type series in each of two systems, in one of which the lines are all triplets, in the other singlets. In addition, the spectrum of the ionized element is rather readily produced, giving rise to an independent but similar system, this time of pairs, as one might expect, since, with one electron gone, the atomic structure of this family should resemble that of the sodium family. In each system combination series occur, and they are apparently more important with the heavier elements, which give the richer spectra. Inter-system combination series are here first met with, as mentioned above. There are other features of these spectra as yet unexplained, and in some cases our knowledge is

far from complete. For instance, well known as the spectrum of Hg is supposed to be, its pair system has not yet been studied.

The Inert Gases, He, Ne, etc.—The spectrum of *Helium* likewise contains two related systems of series, in this case observed as pairs and singlets, but perhaps really more complex, as well as an unrelated system (pairs) of lines produced by ionized helium. The atom of He probably possesses two external electrons, or perhaps only two altogether. On this account its spectrum ought to have a form similar to that of the other elements which have this structural feature, viz., to Mg, etc. This is the case. If one of these electrons were removed, the atomic structure should bear an external resemblance to that of hydrogen, and in fact the spectrum of ionized He consists of one series, following the Balmer formula, and repeated, exactly as is that of H, in two other parts of the spectrum, with fair prospects of the discovery, eventually, of still more of these parallel series. There is a difference, however, shared by the series of ionized Mg, Ca, etc., that 4N must be used instead of N itself in the series formula, and Bohr's theory explains this as due to the presence of the extra, unbalanced charge on the nucleus of the atom.

When we pass to Neon, however, we are dealing, following the fruitful atomic theory of Lewis and Langmuir, with a cubical atom, whose vibrations would be expected to be very complex. As a matter of fact this is the case, and only recently has this spectrum been successfully attacked, in a masterly memoir by Paschen. He finds one series system, but each "term" of each series is really very complex, consisting perhaps of ten widely separated lines, shrinking, however, on passing out along the series, though not in any simple manner. The spectrum of ionized Neon has not yet been identified, and the complexity of its ordinary spectrum is such that it is doubtful if we yet know all about it. Argon is equally rich in lines, and the study of its spectrum is apparently yielding results somewhat similar to those for Ne.

The Cu, Ag, Au Group.—These spectra combine the features of the Na group (pair system) with some of the characteristics of Ne and A, and they have not yet been adequately studied. The spectra of the ionized elements have not been clearly isolated.

The Al, In, Tl Group.—Passing next to the Al group, we return to pair systems as in Na, but the spectra of the ionized elements contain systems of triplets and singlets, which one would expect by analogy to resemble the ordinary (un-ionized)

spectra of the Ca group. The pair systems are fairly well known, the others practically unknown; they lie among the short wavelengths, as one might anticipate from the fact that the forces in an unbalanced system should be greater, and therefore the rates of vibration more rapid.

The Elements of the Carbon Group.—The spectra of C and Si show definite signs of series, but none have as yet been published. Analogy indicates that the ordinary spectra should contain two related systems of series, perhaps of singlets and triplets, and that the ionized element should give a single system, perhaps of pairs. The latter spectrum should be easy to obtain, and therefore difficult to separate from the former.

The other elements in this column show parallel groups of lines, scattered at what seem to be random intervals. The analysis of the spectrum of Neon, which seemed to contain such groups, but was shown to be made up of series, leads us to hope that a similar result will be found to hold in these cases also, but the work has not yet been carried out. These groups constitute what has been called the "second type of regularity" in spectra.

The Elements of the Nitrogen Group.—The same remarks may be made in regard to this family of elements as apply to the preceding, except that one would expect the arrangement of the ordinary spectrum and the spectrum of the ionized element to be interchanged. No series have as yet been worked out here, but obvious triplets and pairs occur in N. The heavier elements contain parallel groups.

The Elements of the Oxygen Group.—The Oxygen family contains two systems of series, pairs and triplets, which seem both to come from the ordinary atom. Apparently the spectrum of the ionized element is the "spark" spectrum, which is well known, but rather complex, and in which no regularities have as yet been found.

The Elements of the Chlorine Group.—These give complex spectra most of which have not yet shown any systematic arrangement, though Paschen has very recently shown that ionized Cl gives series of triplets.

The Fe-Pt Elements.—These elements also give very complex spectra, though a patient analysis of a few of them has yielded parallel groups. It seems at present quite hopeless to attempt to arrange these spectra into series.

This brief survey of our knowledge of spectrum series serves

to show quite clearly how limited that knowledge is, and how urgent is the need for more workers in this important field. Every new source of light, or mode of excitation, at once opens up an extensive field of experimental investigation, as it should be tried out for all possible elements in all possible parts of the spectrum. Last year at least two such modes of excitation were developed which have great interest: the high-vacuum spark used by Millikan to break new ground among the shortest wave-lengths, and the method of explosion of very thin wires used by Anderson. Each of these promises to yield interesting new spectra, and should be most carefully studied from a series standpoint. Other methods will doubtless be developed in the future.

A general review of the series spectra of the elements yields two new laws, recently stated by Kossel and Sommerfeld on the basis of evidence still incomplete, though their probable validity has long been recognized.

The first of these is that the spectrum of an ionized element (lacking one electron) is like that of the element in the next column to the left in Mendelejeff's table, though shifted toward higher frequencies; for example, ionized Ca (Ca') gives a spectrum very like that of K; and this would be expected since each has but one external electron.

The second law states that the spectra alternate in character in passing across Mendelejeff's table. Thus the spectra of Na and Al consist of pair series and resemble each other closely; N is probably similar. Ca, Si and S have many features in common, and each probably furnishes two sets of series, singlets and triplets. This could not be foreseen from considerations of atomic structure, but indicates that when electrons are added to the outside of an atom, as occurs in passing from left to right across the table, the electrons have a strong tendency to unite into rather inactive pairs; thus the spectrum of Al appears to be that due to a single external electron, though there must be three present; but two of these are so closely bound together that they do not take part in the emission of light. Langmuir has recently called attention to this tendency of electrons to form pairs, on the basis of quite different evidence. That other laws of general interest will come out of such study cannot be doubted, and it is earnestly hoped that the near future will witness a vigorous development of this subject.

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